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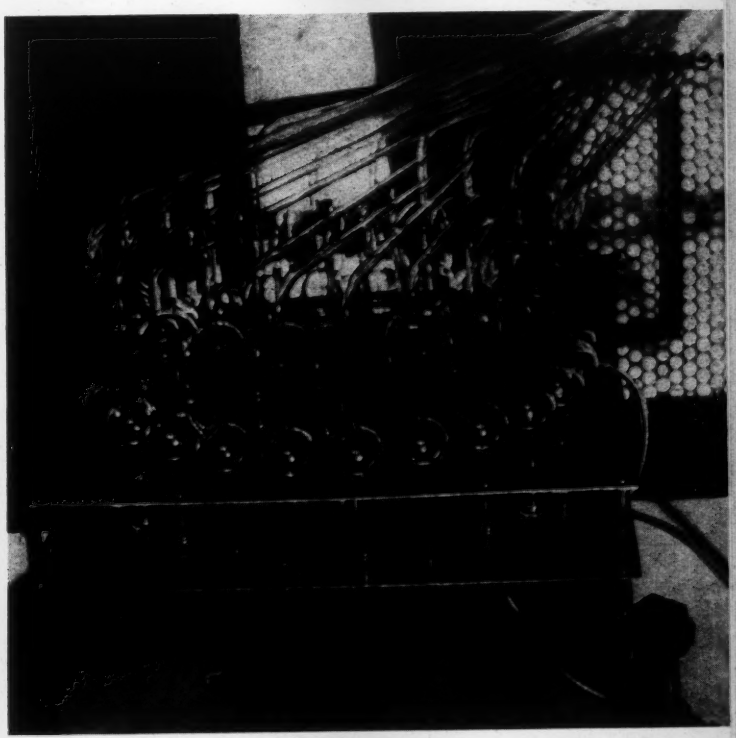

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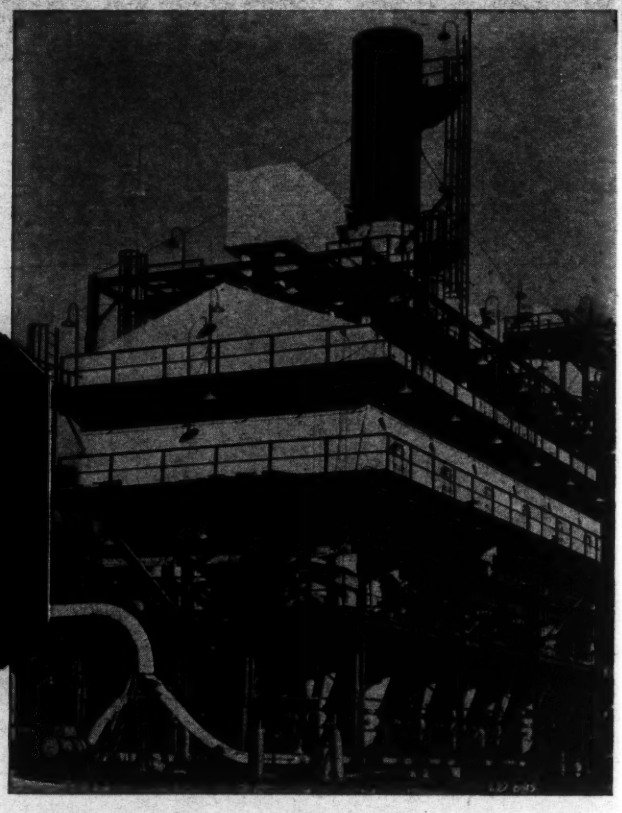

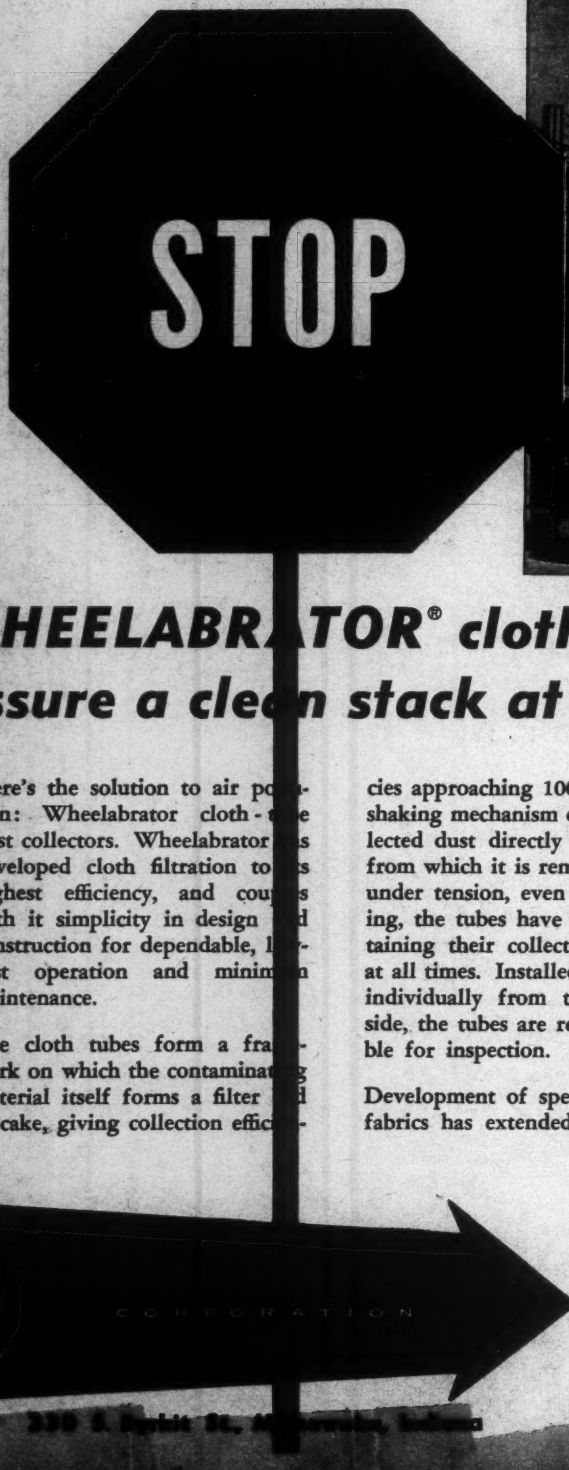

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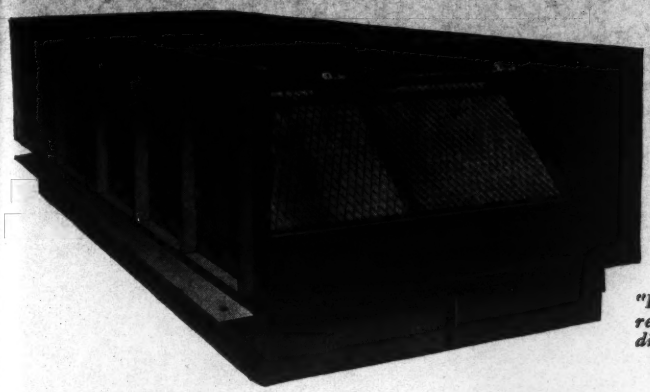

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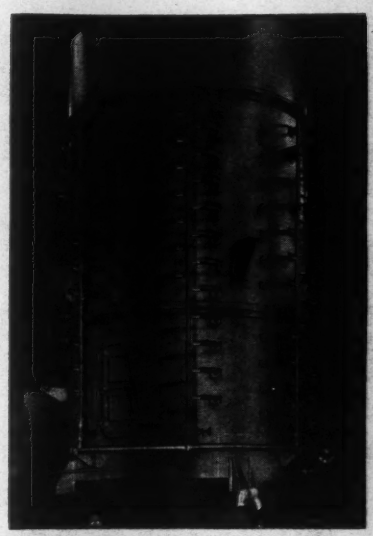

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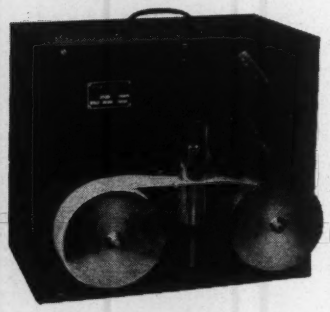

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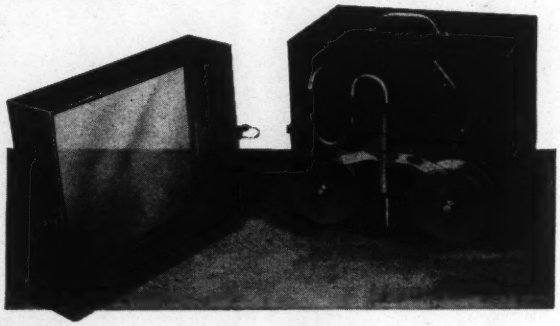

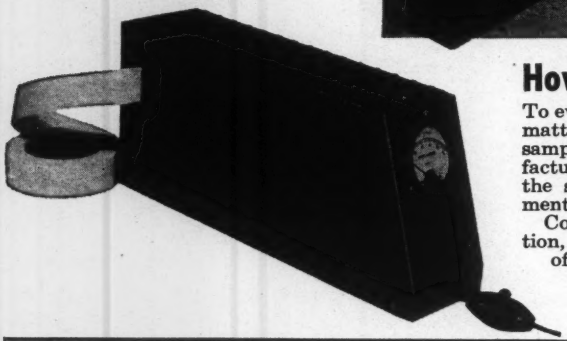

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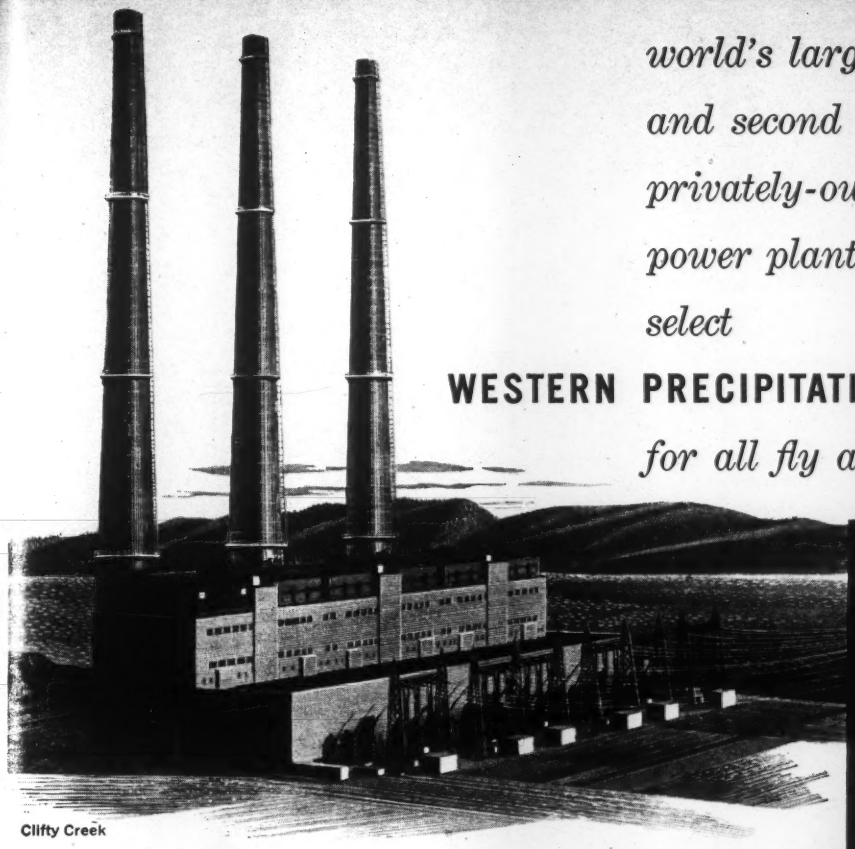
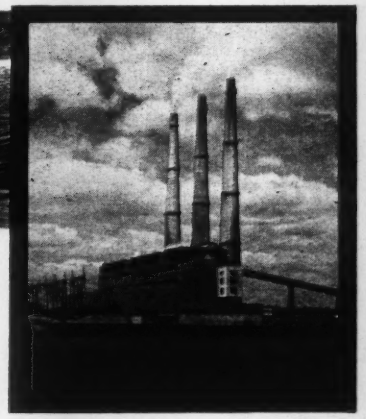


Clifty Creek



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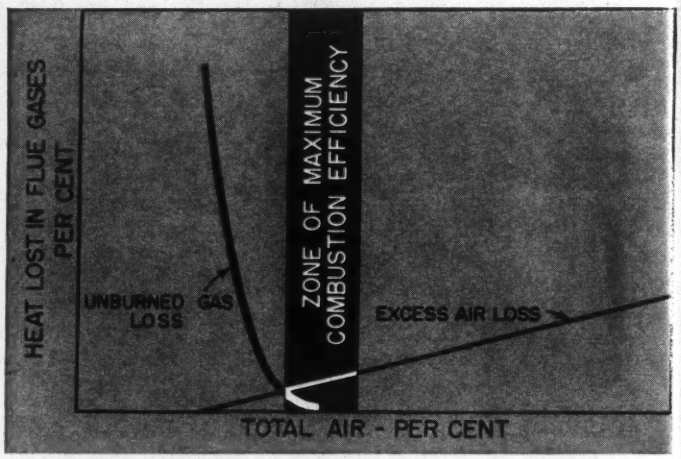
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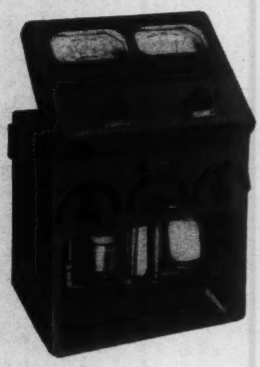

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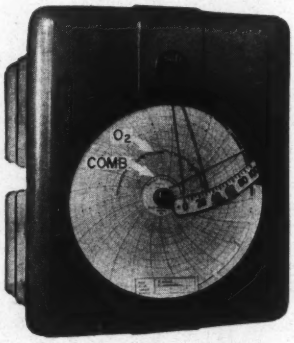

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The Editor welcomes writers interested in air pollution problems and encourages them to use the pages of this journal for the expression of their opinions. But neither he nor the Association assumes responsibility for the validity of the opinions expressed herein.

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AIR POLLUTION...
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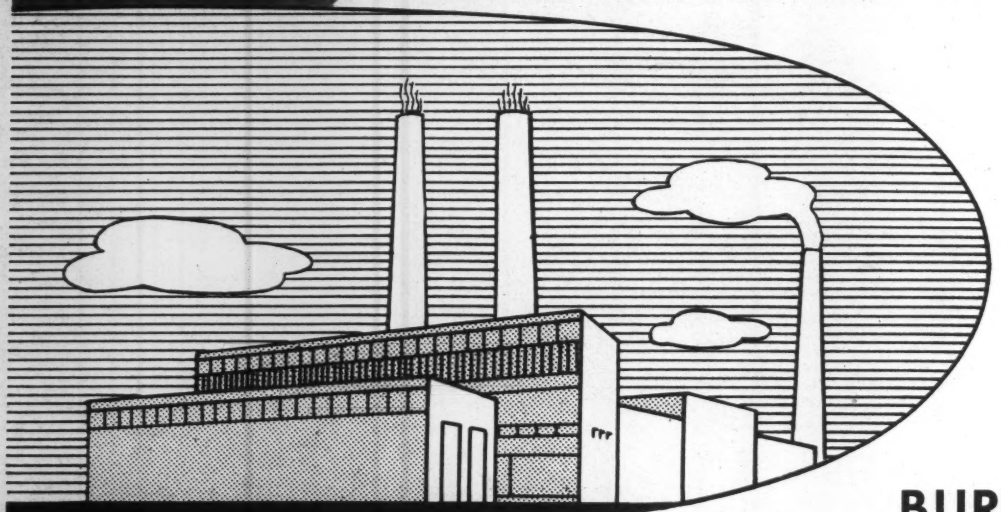

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b . . . Location of incinerator? Air supply?

c . . . How will wastes be handled? How charged?

d . . . Operating schedule?

e . . . Will surroundings dictate minimum height of stack?

f . . . Local codes and ordinances?

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Nitrogen Oxides, Combustion, and Engine Deposits*†

R. S. SPINDT, COURT L. WOLFE and DONALD R. STEVENS

Mellon Institute of Industrial Research
Pittsburgh, Pa.

Engine deposits generally have been pictured as a result of hydrocarbon oxidation reactions accompanied by polymerization and condensation involving both fuel and lubricant. This paper introduces evidence that reactions of unsaturated fuel constituents with oxides of nitrogen formed during combustion, also play an important part in formation of these deposits. Supporting evidence for this hypothesis has been obtained by evaluating influence of engine operating variables on the fixation of nitrogen and by experiments devised to show the effect of these oxides on the formation of engine deposits.

That nitrogen oxides are formed in an engine is not a new observation. Hanson and Egerton[1] studied formation of nitrogen oxides during combustion. Observing the formation of resins when fresh lubricating oils were treated with diluted nitrogen dioxide, they assumed this gas acted as an oxidation catalyst. Graefe[2] found nitro-hydrocarbons in used lubricating oils; Ehlers[3] made similar observations and recognized nitric acid in oils removed from heavy duty trucks. Diamond, Kennedy, and Larson[4] found nitrogen dioxide, as such, did not induce the formation of varnish in a motored engine in the absence of fuels. Walker and O'Hara[5] have used a mass spectrometer to study nitric oxide content of engine exhaust gas and its variation with speed.

It is known in the coke oven gas industry that one type of gum deposit forming in meters and burner orifices is the result of a reaction of nitrogen dioxide with unsaturated constituents in the gas (vapor phase gum[6]). This type of gum contains 3 to 5 % nitrogen, and it has many of the chemical characteristics of engine varnish.

Ed. Note. This paper was originally prepared, as indicated by the title, for an entirely different purpose than potential air pollution from a gasoline engine. Originally, it included (a) the discussion of the data on engine deposits obtained in operations with several base fuels alone and in presence of added nitrogen dioxide and (b) an explanation of the part played by nitrogen oxides in the mechanism of varnish and lacquer formation taking place in automotive crankcases. Therefore, a major portion of this paper is submitted to our readers. ***—Editor***

Recognition of Nitrogen Compounds In Deposits

The idea oxides of nitrogen could play a part in deposit formation came first from a rather broad study of the composition of a wide variety of engine deposit materials. Nitrogen analysis of hundreds of engine deposits of various types showed this element was always present, sometimes in amounts as high as 4%. Deposits formed at high operating temperatures showed a lower nitrogen content (maximum 2%) than those formed at lower temperatures. Some typical figures for nitrogen contents are given in Table I.

Analyses of representative low temperature engine resins indicate there is approximately one atom of nitrogen/molecule of varnish. Neither the original fuels nor oils contain enough nitrogen to account for the amount found in these deposits. However, sufficient oxides of nitrogen are available from the combustion process to be a potential source for the nitrogen found in engine resins.

With development of an analytical procedure[7] for aliphatic nitro compounds, data were obtained indicating the nitro group was present in most of the engine resins. Averaged results given

TABLE I
Nitrogen Content of Engine Resins

High Temperature Deposits	%, Nitrogen
Diesel	
piston	2.0
intake valve	1.4
Aircraft	
piston	1.2
intake valve	0.3
Truck	
piston	0.3
oil screen	1.3
Laboratory L-4 test	
piston	0.6
pentane-insoluble from oil	1.3
Low Temperature Deposits	
Passenger car	
piston	2.7
intake port	3.5
ring groove	2.2
pentane-insoluble from oil	2.4
Laboratory FL-2 test	
piston	1.8
crankcase	2.4
pentane-insoluble from oil	2.7

[1] T. K. Hanson and A. C. Egerton. *Proc. Roy. Soc.* (London), A163, **90** (1937), Inst. of Mech. Eng., Lubricating Discussion, Oct. 1937, Group IV, p. 334.

[2] E. Graefe, *Petroleum Z.*, **28**, No. 23, *Motorenbetrieb u Maschinen-Schmierung*, 5, No. 6, 5 (1932).

[3] K. Ehlers. *Petroleum Z.*, **28**, No. 41; *Motorenbetrieb*, **5**, No. 10, 8 (1932); *Ibid.*, 31, No. 15; *Motorenbetrieb*, **8**, No. 4, 2 (1935); *Ibid.* **34**, No. 19; *Motorenbetrieb*, 9, No. 5, 2 (1938).

[4] Diamond, Kennedy, and Larson. Investigation of Deposition and Oil Deterioration Phenomena in a Motored Engine—Preprint Petroleum Div., *Am. Chem. Soc.*, (New York) 147 (Sept. 6, 1947).

† Published SAE Trans. 64, 797 (1956).

* Presented at National Meeting, SAE Fuels and Lubricants Activity, Philadelphia, Pa., Nov. 9, 1955.

[5] J. H. Walker and C. L. O'Hara, *Anal. Chem.* 27, 825 (1955).

[6] C. W. Jordan, A. L. Ward and W. H. Fulweiler. *Ind. and Eng. Chem.* **24**, 969, 1238 (1932); *ibid.* **25**, 1234 (1933); *ibid.* **26**, 947, 1028 (1934); *ibid.* **27**, 1180 (1935).

[7] Sweet, Spindt and Meyer. A New Method for the Determination of Aliphatic Nitro Compounds. Petroleum Div. Preprints, *Am. Chem. Soc.* (Minneapolis) p. 33 (Sept. 1955).

TABLE II

Average Nitrogen Content of Piston Deposits from Two Types of Operation

Ratio Nitro Nitrogen to Total Nitrogen, %	L-4 Test Conditions	FL-2 Test Conditions
	1.00	3.78
Total Nitrogen, % (Dumas)	0.09	0.65
Nitrogen in Nitro Groups, %	9	17

(a) Deposits obtained from the 2-cylinder test engine.

in Table II based on deposits from the laboratory test engine, show both the total nitrogen and the nitrogen in nitro groups (as determined by the method mentioned) vary with operating conditions in the engine.

A further proof of the existence of the nitro groups in engine resins was obtained from infrared spectra. A characteristic absorption peak is observed at about 6.4 to 6.5 μ which has been identified in spectra of aliphatic nitro compounds. An example is given in Fig. A.

Engine Production of Nitrogen Oxides

To understand better the formation of oxides of nitrogen in an engine, 2 approaches to the problem were followed:

(a) A theoretical study of kinetics of the reaction was made to show the amounts of nitric oxide actually found were predictable. Further calculations were used to interpret effects of different variables.

(b) Experimental studies were conducted with both single and multiple cylinder engines to determine how the concentration of nitrogen oxides in the exhaust gas varied with conditions. Chemical analysis of the exhaust gas verified theoretical conclusions that appreciable nitric oxide should be formed in the combustion process.

Theoretical Studies

The theoretical study of nitrogen fixation, details of which are given in Appendix I, may briefly be described as an evaluation of the time, temperature and pressure relations acting on the reactants, nitrogen and oxygen, according to the following equation:

$$N_2 + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2NO \qquad (1)$$

A knowledge of the intake pressure (a measure of engine load) air-fuel ratio, and engine compression ratio makes it possible to compute the gas concentration and a theoretical average flame temperature. The rate constant for the reaction can be computed from the flame

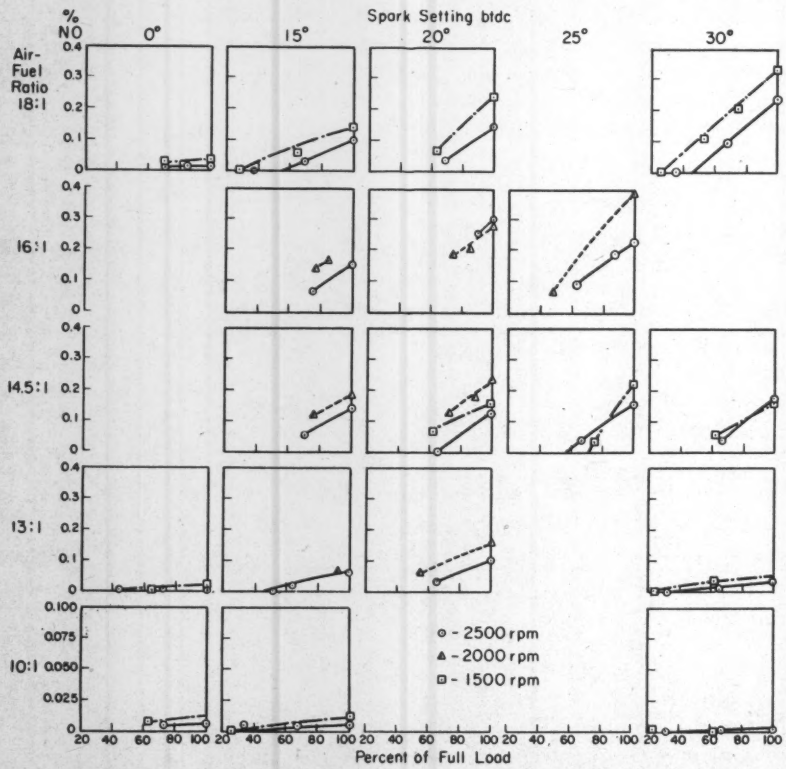

Fig. B. Effect of operating conditions on the content of nitric oxide in the exhaust gas.

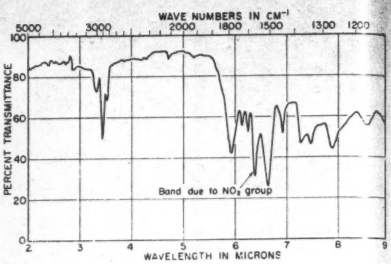

Fig. A. Infrared absorption spectrum of characteristic low temperature engine deposits.

temperature. It is therefore possible to estimate the nitric oxide concentration from equation (2). A discussion of this equation is given in Appendix I.

$$(NO) = K\sqrt{(N_2)\ (O_2)} \qquad (2)$$

$$\tanh K_2 K t \sqrt{(N_2)\ (O_2)}$$

where

NO, N_2, O_2 represents concentrations of nitric oxide, nitrogen and oxygen, respectively,

K is the square root of the equilibrium constant of equation (1); it is obtained from thermodynamic data,

k_2 is the rate constant for the decomposition of NO, in cc./mole/sec.,

t is time in seconds.

By varying intake pressure, at constant air-fuel ratio and compression ratio, a family of curves can be obtained for different time intervals (Fig. F and G). From these curves, comparisons can be made with experimentally-found nitric oxide concentrations in order to determine whether the time factor for the reaction is of the same order of magnitude as that estimated to be available in the engine. Results of these calculations show the flame temperature is adequate to cause nitrogen fixation, that the reaction will take place if oxygen is present in excess, and that sufficient time is available to account for the nitrogen oxides actually found.

Experimental Engine Studies

In a gasoline engine combustion can occur successfully over a wide range of air-fuel ratios. Maximum power is produced at about 12.5:1, while compositions theoretically correct for complete combustion, are about 14.5:1 depending on the fuel. Since gasoline economy is achieved at high air-fuel ratios, manufacturers have endeavored to improve engine performance under lean conditions. Even as early as 1941[8] air-fuel ratios had reached an average of 15.5:1.

[8] W. G. Lovell, J. M. Campbell, B. A. D'Alleva and P. K. Winter. *S.A.E. Trans.*, **48**, 160 (Apr. 1941).

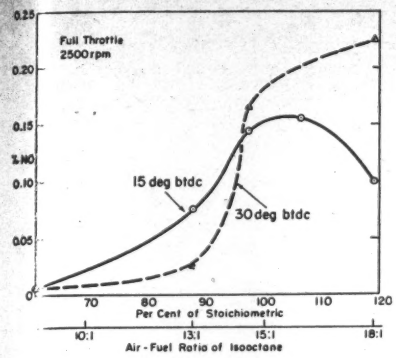

Fig C. Correlation of exhaust nitric oxide with air-fuel ratio at 2 spark settings.

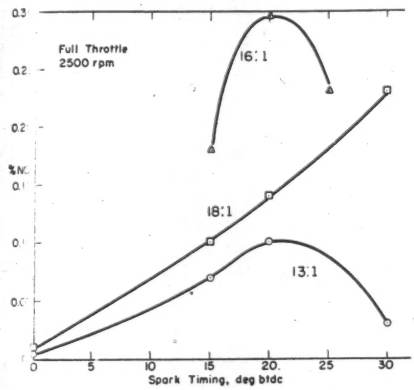

Fig. D. Correlation of exhaust nitric oxide with spark timing at three air-fuel ratios.

Experimental data on the nitrogen oxide content of exhaust gases were obtained by operating the test engine (Appendix III) under systematically varied conditions of speed, torque, spark timing, and air-fuel ratio. The exhaust gases were sampled and analyzed for nitrogen oxides as described in Appendix II. Isooctane was used as the fuel to eliminate complications that might arise from engine knock. This is justified, since fuel type has been found to have little effect on the extent of nitrogen fixation.

The data in Fig. B show conditions employed and trend of results. These data are difficult to analyze due to the complex inter-relations of the variables. One important conclusion to be drawn from this figure is that nitric oxide always increases with increasing intake pressure, as reflected in engine load, independent of any other fixed variable. In general, the effect of increasing speed is to reduce the amount of nitric oxide formed because of the decrease in reaction time.

Some of the data contained in Fig. B are also the basis for Fig. C and D. Fig. C correlates the % nitric oxide with air-

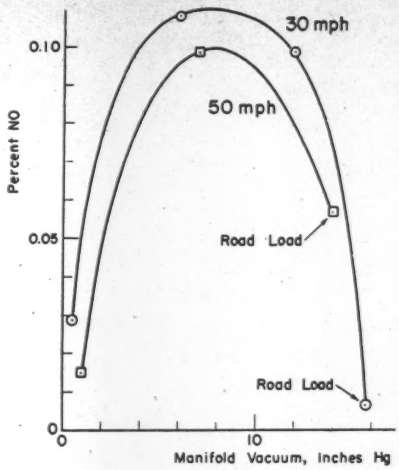

Fig. E. Nitric oxide in exhaust gases from a conventional automobile as a function of manifold vacuum.

fuel ratio for two spark settings which bracket optimum engine performance. At rich mixtures, little fixation occurs because of the lack of oxygen. At 15 deg. btdc.[10] and 84% of stoichiometric mixture, (13:1) nitrogen fixation occurs in spite of the slightly reducing atmosphere whereas at 30 deg. btdc. the increased time available results in a loss of nitric oxide as a result of reduction. At 100% of stoichiometric, both curves indicate appreciable fixation has occured. Above 100% stoichiometric, the 15 deg. btdc. curve reaches a maximum and starts to decrease because of lower flame temperatures occurring at lean mixtures, with the resulting lower reaction rate. The increased time available at 30 deg. btdc. results in a continuing mild increase in the amount of nitric oxide formed.

Fig. D correlates nitric oxide in the exhaust gas with spark timing at three air-fuel mixtures. Spark timing affects both the time available and the temperatures to which the combustion chamber gases are subjected. At rich mixtures, as exemplified by the curve for 13:1 air-fuel ratio, there is a gradual increase in nitric oxide production up to the optimum spark timing; at more advanced timing the reducing atmosphere tends to destroy nitric oxide previously formed.

At slightly lean mixtures, as illustrated by 16:1 air-fuel ratio, the amount formed has increased rapidly near optimum spark timing. It is in this range that the rate of fixation is greatest. At lean mixtures, 18:1 and greater, rate of formation is slower because of lower flame temperatures. However, production continues at the more advanced timing be-

[10] Degrees before top dead center.

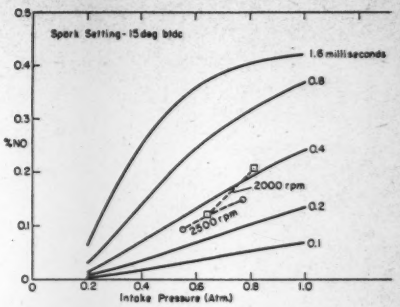

Fig. F. Theoretical nitric oxide formation as a function of pressure and time. Oxygen concentration in exhaust gas —0.5%

cause of excess oxygen and increased time available.

While experimental results on the effect of compression ratio were not obtained, the theoretical studies show increasing this variable should result in higher combustion temperatures and consequently a greater extent of nitrogen fixation would be expected.

A preliminary dynamometer test was run using a passenger car to evaluate the concentration of nitrogen oxides in the exhaust gas under simulated field conditions. Data were obtained at 2 car speeds for several different manifold vacua; engine torque and air-fuel ratios were also measured. The air-fuel ratio was found to be approximately 16:1 under part throttle conditions; at full throttle it was 12.5:1. Fig. E illustrates these data on the nitric oxide content of exhaust gases.

The amount of nitric oxide present is controlled by throttle settling and air-fuel ratio. The amount is low at full throttle, rich mixture conditions, but increases at part throttle due to leaning out of the mixture. After passing through a maximum, it decreases with increasing manifold vacuum in the engine.. At 50 mph., where road load is appreciably greater than at 30 mph., more nitric oxide is found than at the lower speed. Although these data were obtained from only one vehicle, they suggest many cars may be operating under conditions of high nitric oxide formation much of the time.

It is concluded engines operating under normal spark timings with mixtures on the lean side of stoichiometric will produce appreciable nitric oxide, the amount formed depending most directly on the load applied. There appears to be little hope for a reduction in nitrogen oxides from changes in engine conditions, since optimum economical operation seems to be in the range of high nitrogen fixation. That these oxides of nitrogen can lead to piston and crank-

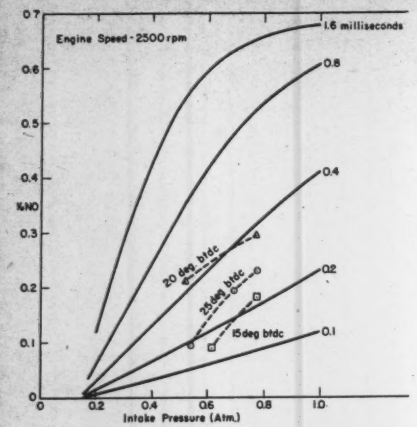

Fig. G. Theoretical nitric oxide formation as a function of pressure and time. Oxygen concentration in exhaust gas —2%.

case deposits has been shown by repeated engine tests.

Engine Experiments With High and Low Nitric Oxide Production

Low temperature tests were made using equipment described in Appendix III to evaluate engine conditions, set to produce high and low nitrogen fixation, for their effect on deposits from different fuels. The fuels used were a clean, non-depositing straight-run gasoline, and thermally and catalytically cracked distillates which are known to be deposit-forming. Typical inspection data for the fuels used are given in Appendix IV.

The results, tabulated in Table III, indicate it is difficult to distinguish between any of these fuels when operating at rich mixtures, (11:1) or low nitrogen fixation. On the other hand, when operating at lean mixture (17:1) with approximately 0.25% nitric oxide in the exhaust (well within the range of that produced in practical operation), the cracked gasolines give significantly more deposits. It is clear there is a large difference in the amount of deposits accumulated when using operating procedures resulting in formation of significantly different amounts of nitric oxide. (See Appendix III for a discussion of deposit weights.)

Effect of Added Nitrogen Dioxide On Engine Deposits

A series of engine tests was run to demonstrate nitrogen dioxide can effect an increase in piston varnish.

This gas was chosen because it is known nitric oxide reacts with oxygen to produce the dioxide. The residence time in the crankcase is sufficiently long

TABLE III

Effect of High and Low Nitric Oxide Production on Fuel Deposit Formation

Gasoline	Piston Deposit: Low Nitric Oxide Production 11:1 A/F — CRC Color	Piston Deposit: Low Nitric Oxide Production 11:1 A/F — Acetone Soluble Deposit, mg./in.^{2}	Piston Deposit: High Nitric Oxide Production 17:1 A/F — CRC Color	Piston Deposit: High Nitric Oxide Production 17:1 A/F — Acetone Soluble Deposit, mg./in.^{2}
Straight-run	10	0.05	10	0.01
Thermally-cracked	10	0.10	7	3.85
Catalytically-cracked	9.5	0.10	7	2.06

TABLE IV

Effect of Added Nitrogen Dioxide on Deposit Formation

	Piston Deposit — CRC Color	Piston Deposit — Acetone Soluble Deposit, mg./in.^{2}
Reference	9	0.04
NO_2 added to intake (10 gm./hr.)	3	0.6
NO_2 added to crankcase (51 gm./hr.)	2	1.9

for appreciable conversion, according to the following equation:

$$2NO + O_2 \rightarrow 2NO_2$$

It has been observed exhaust gas, colorless when initially collected, changes on standing as the colored nitrogen dioxide is formed. Further, laboratory experiments have shown reaction products of nitrogen dioxide and gasoline are similar to varnish from the engine. Because of these factors, and the difficulty in handling nitric oxide without introducing unknown amounts of the dioxide, it is believed the experiments using nitrogen dioxide lead to significant information.

A control run using low nitric oxide producing conditions (rich mixture) confirmed (Table IV) that fuel contributed little to engine deposits under these conditions. A second test was made under the same conditions except that nitrogen dioxide was added to the intake manifold at a rate of approximately 10 gm./hr. (0.03% of intake charge) in an attempt to simulate higher rates of nitrogen fixation. In spite of the fact this was a small addition, it resulted in a significant increase in piston varnish. In a third test, the nitrogen dioxide was added to the crankcase of the engine; a notable increase in deposits was again observed.

Engine Operation With A Nitrogen-Free Atmosphere

In order to eliminate formation of nitrogen dioxide during engine operation, test runs were made with an essentially nitrogen-free atmosphere in which the air was replaced by a mixture of oxygen and carbon dioxide. The commercial gases available gave a mixture which still contained 0.1 to 0.5% nitrogen, but the resulting exhaust gas showed on analysis only 0.0004% nitric oxide, about 1/1,000 that formed when operating with normal air under conditions conducive to high nitrogen fixation. Because of the higher specific heat of carbon dioxide these tests were made with the artificial air containing 30 to 35% oxygen; this was necessary in order to provide a flame temperature close to those calculated for normal air. The carburetion was controlled to yield about 5% oxygen in the exhaust. Under these conditions the fuel consumption is 1.5 times that with normal air, indicating high concentrations of both fuel and oxygen. At the end of 39 hr. of low-temperature operation on thermally cracked gasoline, the engine remained very clean, as shown in Table V.

Adding nitrogen dioxide at an average rate of 130 gm./hr. (0.4%) to the intake of the engine running on the artificial atmosphere, however, resulted in heavy varnishing after only 10 hr. of operation. These results in Table VI, indicate, as do those in Table IV, that nitrogen dioxide in the engine does increase deposits . . .

Acknowledgment

The authors wish to acknowledge the continuing interest and encouragement of W. A. Gruse of the Mellon Institute. Thanks are due to J. E. Taylor of the Gulf Research & Development Company for his active interest in this problem. Special thanks are also extended to J. E. Baily, H. T. Edwards, and A. N. Jones for their valuable assistance in conducting the tests.

TABLE V
Effect of an Artificial Nitrogen-Free Atmosphere on Fuel Deposits (Thermally Cracked Gasoline)

	Piston Deposit	
Atmosphere	CRC Color	Acetone Soluble Deposit, mg./in.²
Normal	3	2.4
Artificial	9	0.1

TABLE VI
Effect of Adding Nitrogen Dioxide to an Artificial Atmosphere (Thermally Cracked Gasoline)

Atmosphere	CRC Color	Acetone Soluble Deposit, mg./in.²
Artificial (39 hr.)	9	0.11
Artificial + 0.4% NO_2 (10 hr.)	2	1.9

APPENDIX I

Kinetic Calculations of Nitrogen Fixation

In attempting to estimate the rate of nitric oxide formation in an engine from theoretical considerations, nitrogen is considered to react with oxygen according to a bi-molecular reaction at high temperatures, as given in equation (1).

$$N_2 + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2NO \qquad (1)$$

Even though some authorities believe the reaction may proceed through a chain mechanism, it is not considered desirable to include any consideration of such reactions in this study, because of the critical simplifying assumptions which had to be made. Therefore, the following simplified rate equation accounts for the nitric oxide formation:

$$\frac{d(NO)}{dt} = k_1 (N_2)(O_2) - k_2(NO)^2 \qquad (2)$$

In this equation, the nitrogen concentration has been assumed to be essentially constant. Further, since there is no practical way to determine the initial concentration of oxygen, this concentration is also assumed to remain constant, and it is calculated from the percentage of oxygen remaining in the final exhaust gas. A more rigorous derivation leads to an integrated equation of the same form, so that errors in computations are of degree rather than kind. Integration leads to an expression of the nitric oxide concentration in terms of the oxygen and nitrogen concentration, time and the reaction equilibrium and rate constants, which are functions of the temperature.

$$(NO) = K\sqrt{(N_2)(O_2)}\tanh k_2 Kt\ \sqrt{(N_2)(O_2)} \qquad (3)$$

Additional simplifying assumptions required are:

(A) Gas concentrations are computed using the perfect gas law from the intake gas pressure, temperature, the residual exhaust gas temperature and pressure, and the compression ratio for the condition with the piston at tdc.

(B) Combustion is assumed to occur instantaneously throughout the mixture, so that the gas is at a uniform temperature for the time intervals under consideration.

(C) No account is taken of self-heating in the first-portion of the gas to burn.[11]

(D) No account is taken of dissociation in the burned gas.

With these restrictions, the following equations define the oxygen and nitrogen concentrations and flame temperature.[12]

$$(O_2) = \frac{\%O_2 P_i}{100RT_i}\left[CR - (P_i/P_e)^{-1/Gamma}\right] mole/cc. \qquad (4)$$

$$(N_2) = \frac{\%N_2 P_i}{100RT_i}\left[CR - (P_i/P_e)^{-1/Gamma}\right] mole/cc. \qquad (5)$$

$$T_f = \frac{(T_e/T_i)(P_i/P_e)\left[CR - (P_i/P_e)^{-1/Gamma}\right]\left[T_i\, CR^{Gamma-1} + \Delta H/C_v M_e\right] + T_e\, CR^{Gamma-1}}{(T_e/T_i)(P_i/P_e)\left[CR - (P_i/P_e)^{-1/Gamma}\right] + 1} \qquad (6)$$

where:

P_e — exhaust gas pressure, atm.

P_i — intake gas pressure in cylinder, atm.

T_e — residual exhaust gas temperature, deg. K

T_i — intake gas temperature, deg. K

CR — engine compression ratio

R — gas constant, ml. atm.

γ — ratio of specific heats at constant pressure and constant vol.

C_v — specific heat at constant volume, cal./mole/deg. K

ΔH — heat of combustion of one mole of fuel, cal.

M_e — total moles of gas/mole of fuel

The temperature equation is derived from the following expression in terms of the mixing temperatures, compression temperature, and the heat released on combustion

$$T_f = \frac{m_i T_i + m_e T_e}{m_i + m_e}\,(CR^{Gamma-1}) + \frac{m_i}{m_i + m_e}\cdot\frac{\Delta H}{C_v \cdot M_e} \qquad (7)$$

but if V_c is the combustion chamber vol., V_d is the piston displacement and if V_x is the additional vol. into which the residual exhaust gas expands to bring its pressure down to that of the intake gas, as defined by the relation,

$$P_i(V_c + V_x) = P_e V_c$$

then

$$m_e = \frac{V_c P_e}{RT_e} = \text{moles unscavanged exhaust} \qquad (8)$$

$$m_i = \frac{(V_d - V_x)P_i}{RT_i} = \frac{V_c}{RT_i}\left[CR - (P_i/P_e)^{-1/Gamma}\right]P_i \qquad (9)$$

= moles of intake charge.

Substituting these values for mi and me into equation (7), eliminating the volume term, and rearranging yields equation (6). Having evaluated the theoretical flame temperature, T_f, the rate constants required in equation (2) are obtained from equations (10)[13] and (11) [14]

$$K = 4.36e^{-21500/RT} \qquad (10)$$

$$k_2 = 3.40 \times 10^{12} e^{-40000/RT}\ cc./mole/sec. \qquad (11)$$

The rate of change of temperature in an Otto cycle engine due to expansion, is of the order of 10⁵C/sec. at about 2000 rpm., sufficiently rapid to freeze the reaction and retain most of the nitric oxide formed.[15] The

[11] G. M. Rasweiler and L. W. Withrow. *S.A.E. Journal* **36**, 125 (Apr. 1935).

[12] Developed from equations presented by Lewis and Von Elbe. Explosion, Combustion, and Detonation of Gases. Academic Press (1951).

[13] Rossini. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds. p. 748, A.P.I. Research Project 44, Carnegie Press (1953).

[14] H. S. Glick, W. Squire and A. Hertzberg. A New Shock Tube Technique for the Study of High Temperature Gas Phase Reactions. Fifth Symposium on Combustion. p. 393, Reinhold, New York (1955).

[15] H. Wise and D. I. Baker, *J. Chem Phys.* **21**, 1904 (1953).

time required to expand the charge to the point where this rate of temperature drop occurs is of the order of 0.5 to 5 millisec., depending on the speed of the engine.

Using equation *(3)* the nitric oxide concentration can be evaluated at constant air-fuel ratio and compression ratio for different values of intake pressure. A family of curves is obtained as shown in Fig. F and G for various time intervals. Superimposed on these curves are experimental results which indicate that at high intake pressures, *i.e.* high engine torque, the apparent time of reaction is truly of the order of 1 to 2 milli-sec. Further, these data show at high intake gas pressures the formation of nitric oxide approaches thermodynamic equilibrium for the calculated flame temperature. At low intake gas pressures several factors, such as less turbulence and slower burning velocities, may be operative reducing the rate of fixation from that predicted for a constant reaction time.

It is realized the calculations presented here involve assumptions that may have been oversimplified and results should be taken as tentative only. The principal justification for considering them lies in the fact that the experimentally found concentrations are in accord with theoretical values at time intervals expected to occur in the engine.

APPENDIX II

Analysis of Nitrogen Oxides

As the exhaust gas leaves an engine, the principal oxide of nitrogen present is nitric oxide (NO). This gas at atmospheric temperature slowly forms nitrogen dioxide[16] by reaction with oxygen. A direct determination of either of these gases is difficult. However, a satisfactory indirect chemical analysis has been worked out for the total nitrogen oxides. The method depends on reacting a sample of the gas, still containing principally nitric oxide, with oxygen and an alkaline solution. The oxides of nitrogen are recovered as nitrous acid.

As long as nitric oxide is in excess, the reaction

$$NO + NO_2 + H_2O \rightarrow 2HNO_2 \qquad (12)$$

appears to be sufficiently rapid[17] to control the absorption. If, however, the nitric oxide is first allowed to be converted into nitrogen dioxide, the reaction

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \qquad (13)$$

occurs. It is, therefore, important to treat the sample with the alkaline solution soon after sampling.

The nitrite ion formed is then determined colorimetrically by synthesizing a diazo dye[18, 19, 20]. The method is very sensitive;

[16] J. C. Tracy and Farrington Daniels. *J. Am. Chem. Soc.* **77**, 2033 (1955).
[17] L. G. Wayne and D. M. Yost. *J. Chem. Phys.* **19**, 41-7 (1951).
[18] F. A. Patty and G. M. Petty, Jr. *Ind. Hyg. & Toxic.*, **25**, 361 (1941).
[19] J. A. Shaw. *Ind. Eng. Chem.*, Anal. Ed., **8**, 162 (1936).
[20] Seil. Gas Chemists Manual of Dry Box Purification of Gas. Amer. Gas Asso. New York (1943).

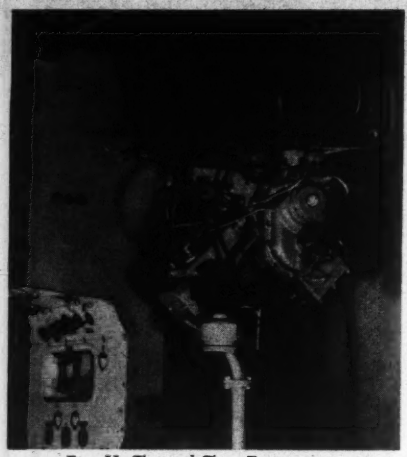

Fig. H. Typical Test Equipment.

amounts as low as 1 x 10^{-9} mole/ml. are easily detected. Therefore, the procedure can be applied to the analysis of gases containing extremely small quantities of nitrogen oxides.

The method has been checked against synthetic gas mixtures of nitrogen and nitric oxide. The following results have been obtained.

Concentration of Nitric Oxide, Volume %

In Gas Mixture	Found
0.107	0.115
0.25	0.255
0.567	0.505, 0.505

The procedure as finally adopted in this laboratory is as follows:

Analytical Procedure

A 100 ml. gas sample, dried over phosphorous pentoxide, is collected over mercury in a gas burrette and transferred quantitatively to a clean, dried, evacuated 150 ml. separatory funnel containing 25 ml. of 10% sodium hydroxide solution. Oxygen is added to 1 in. of mercury pressure. The funnel is then shaken for 15 min. on a wrist-action shaker to remove the nitric oxide by reaction 12.

An aliquot of this solution is treated with Greiss reagent[20] to develop the diazo dye. For concentrations of nitrogen oxides in the gas above 0.2%, 10 ml. of the alkaline solution are first diluted to 100 ml. with distilled water. The determination is completed by measuring the absorbance of the dye solution

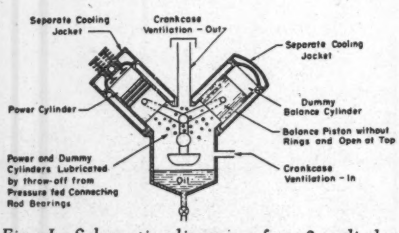
Separate Cooling Jacket
Crankcase Ventilation – Out
Separate Cooling Jacket
Power Cylinder
Dummy Balance Cylinder
Balance Piston without Rings and Open at Top
Power and Dummy Cylinders Lubricated by throw-off from Pressure fed Connecting Rod Bearings
Crankcase Ventilation – In
Oil

Fig. I. Schematic diagram of a 2 cylinder test engine.

and comparing it with a solution prepared with standard sodium nitrite. Because sodium ion concentration was found to affect the development of the dye color it is necessary to determine the absorbance of the solution containing standard nitrite at the same sodium ion concentration employed with the sample.

The calculations for concentration in the gas are as follows:

$$\% NO_2 = \frac{A_s}{A_{st}} \frac{C_{st} \cdot D \cdot V_s \times 22{,}400 \times 100}{V_g}$$

$$= \frac{A_s \cdot C_{st} \cdot D \cdot V_s \times 2.24 \times 10^6}{A_{st} \cdot V_g} \qquad (14)$$

Where

A_s = absorbance of sample
A_{st} = absorbance of standard solution
C_{st} = concentration of standard in moles/ml.
D = dilution factor = ml. of dye solution/ml. of alkaline solution
V_s = vol. of alkaline solution, ml.
V_g = vol. of gas corrected to standard conditions, ml.

APPENDIX III

Apparatus

Most of the engine experiments were conducted using a 2-cylinder test engine. A typical test unit, shown in Fig. H, has been described in detail by others[9, 21, 22]. Briefly, this engine is a 2-cylinder V-type 4-cycle gasoline engine especially designed for research purposes. Two separate lubricating systems are employed, one for the valve train and the other for the piston, connecting rod, and crankshaft bearings. For the research program described, only phenomena occurring in the crankcase oiling system is considered.

In order to gain additional data, one of the pistons has been replaced by a balancing assembly shown in the schematic diagram, Fig I. This balancing member is made from a standard piston except that the head is cut out and the ring grooves are eliminated. Oil-

TABLE VII

Speed, rpm.	1500-2500
Load, lb.-ft.	O—Maximum
Air-fuel ratio	10:1—18:1
Spark advance, deg. btdc.	0—30
Coolant temperature, °F.	90
Oil temperature, °F.	160
Oil charge, gm.	500
Test duration, hr.	10—40
Compression ratio	6.5:1—1.5:1

[9] R. S. Spindt and C. L. Wolfe. The Where and Why of Engine Deposits. SAE West Coast Meeting (August 1951).
[21] Jacobson, *Petrol. Eng.* **15**, No. 8, p. 196-8 (May 1944).
[22] C. W. Butler, The Gulf Two-Cylinder Test Engine, Coordinating Research Council Symposium on Laboratory Oil Test Engines, p. 23-41 (Nov. 3, 1949).

laden vapors from the crankcase pass back and forth through this unit. The end of this assembly is closed with a conventional head. A heavy coating of varnish builds up on both the sliding unit and the cylinder wall. In other respects, the engine is quite conventional, relative to control and instrumentation.

Displacement of the engine is 42.1 in.³ Compression ratio may be varied by changing heads. Engine variables were controlled within the ranges given in Table VII.

All engine tests were conducted with uncompounded lubricating oils to eliminate any effects attributable to the use of additives. Unleaded refinery distillates, typical of commercial gasoline base stocks, were employed. Work in this laboratory had previously indicated that tetraethyl lead does not significantly change the amount of resin formed.

Upon completion of each test, both power and balance pistons were rated visually following the standard C.R.C. procedure. However, to obtain an objective measure of the deposits, the varnish was removed with acetone and separated into insoluble and soluble fractions by centrifuging. Both fractions were then recovered, weighed, and reported in terms of mg./in.² Relatively little insoluble material is obtained when operating on these base fuels and oils; therefore, they were not considered in this paper. Even though deposits from all collecting surfaces were evaluated, only data from the power piston are reported.

APPENDIX IV
Inspection Data on Typical Gasoline Distillates Used in This Study

	Mid Continent Raw Thermally Cracked	Raw Fluid Catalytically Cracked	Mid Continent Straight-run	Aviation Alkylate
Specific gravity 60 deg./60 deg.	0.7389	0.7559	0.7121	0.6998
Sulfur, (D1266) %[b]	0.069	0.041	0.025	—
Oxygen stability, (D525) min.[b]	>1440[a]	1260[a]	>1440	>1440
Bromine number (D1159) g./100 g.[b]	70.8	92.8	0.0	—
Olefins, (D875) %[b]	50.2	63.2	0.0	—
Aromatics, (D875) %[b]	1.5	8.8	—	—
Vapor pressure, (D323) lb.[b]	10.3	5.3	—	3.5
Distillation, (D86) % Distilled,[b]	°F			
Initial	92	116	94	125
10%	142	146	139	180
50%	260	246	212	220
90%	355	388	290	251
End	425	428	314	323
Fl-2 rating	75	50	—	98

[a] Gasoline inhibited with di-t-butyl-p-cresol.
[b] Numbers refer to ASTM methods.

Background of Design Criteria For Municipal Incinerators—The Designer's View*

S. A. GREELEY
Greeley and Hanson
Chicago, Ill.

This paper originally included more information than is presented here. It has been excerpted for the Journal and includes only those parts of direct interest to air pollution and its control.
—Editor

The design of municipal incinerators is as difficult a problem as we meet in our practice of sanitary and municipal engineering. There are several reasons; the varying character of the refuse (at present and in the future), lack of precise operating data, and the considerable measure of sales instead of impartial and experienced engineering. In the early days of refuse incineration, 75 to 50 or less yrs. ago, much of the engineering was done by properietors of patents or special processes.

Background and Scope of Design Criteria

The author considers background of design criteria for municipal incinerators to mean local conditions for which bases of design are to be established. These include quantity and kind of refuse for which capacity is to be provided, surface and subsurface conditions at the site, adjacent roadways, climate as affecting the extent of enclosure, environment as affecting the chimney and its discharges, and the type of building suited to the locality.

The scope of design criteria is considered by the author to extend primarily to those things affecting efficiency of operation, such as bases of design of facilities pertaining to combustion, and things affecting operation of furnaces, such as clearances, fly ash-removal facilities and control instruments. Design criteria of the general parts of a municipal incinerator will not be discussed at any length.

TABLE I

Principal Components of a Municipal Incinerator and Costs

Item	Illustrative unit cost/ton of rated capacity
1 Scales, scale house, entrances and exits, maneuvering yard, dumping rail, and enclosing wall	$ 100.00
2 Storage bin	200.00
3 Cranes	225.00
4 Outside flues and fly ash-removal facilities	400.00
5 Chimneys	300.00
6 Miscellaneous items, such as drains, piling, and woodhogs	75.00
7 Furnaces	1,200.00
8 Inside flues	85.00
9 Building and enclosures	1,415.00
Total	$4,000.00

Brief Historical Comment

Municipal refuse incineration began in England in 1874, with construction of a plant to burn mixed refuse at Nottingham. In the U. S., first incinerators were built for garbage disposal, one having been designed by H. G. Reilly for the U. S. Government on Governor's Island, 1885. Between that time and about 1900, a number of incinerators were designed and built, chiefly for incineration of garbage with some auxiliary fuel. Municipal incineration of mixed refuse

* Excerpts from a paper presented at the semiannual meeting, ASME, Cleveland, Ohio, June 17-21, 1956.

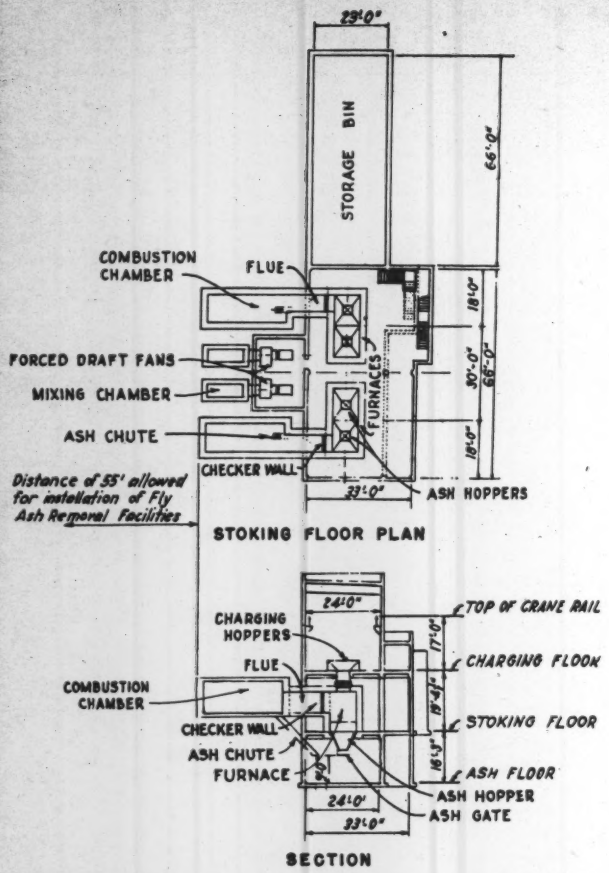

Fig. 1. Plan and section designated in 1950 as a manually stoked rectangular furnace. Stoking would be largely accomplished by oscillating or moving grates like those first used at Baltimore.

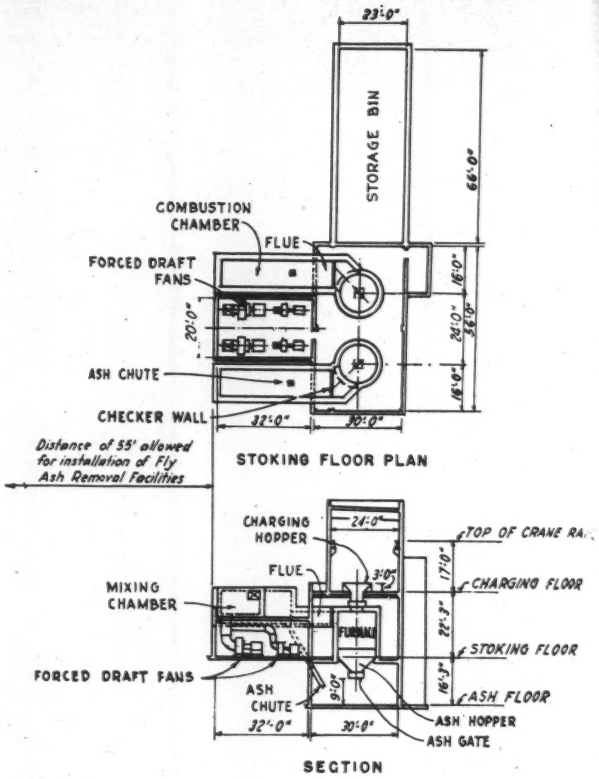

Fig. 2. Plan and section of mechanically stoked round furnace.

as practiced in England and to some extent on the continent, was given stimulation by the installation of a plant at West New Brighton, N. Y., under the administration of John T. Fetherston, and one at Milwaukee from plans and specifications by Rudolph Hering, both about 1910. Since then development of municipal refuse incineration has been rapid. Recently design has been influenced by efforts to reduce air pollution and by an increase in heat content and decrease in unit weight of refuse materials.

Parts of a Municipal Incinerator

Of a complete municipal incinerator, about 40% of the cost is for furnaces and appurtenances, and about 60% for approaches, storage bin, building, and chimney. Major parts are listed in Table I.

Kinds of Furnaces

In municipal incinerators there are many kinds of furnaces, some are round and others rectangular in plan. There are numerous departures, such as revolving cylinders and vertical or high furnace structures. Most of these different kinds have been developed and promoted by manufacturing concerns, accounting for considerable variety. Five different kinds are shown in Fig. 1 to 5. Each furnace was specified to have a rated capacity of 100 tons of rubbish/24 hr.

Description of the Designer

There are 3 kinds of designers active in refuse incineration practice as follows:

(1) The designer in a public works office—public designer. This kind is illustrated by those in New York City who have completely designed several large incinerators.

(2) The designer in private practice —a private practicing engineer.

(3) The designer associated with a manufacturing company—a proprietary designer. Generally this kind designs only the furnace and its appurtenances which the manufacturer promotes, sometimes under a patent or alleged patent. Many refuse incinerators have been acquired by municipalities under designs of this kind.

Sometimes the complete design is prepared by the public or private designer and the proprietary designer jointly. The latter designs the furnace and its appurtenances to fit the building and chimney designed by others in accordance with detailed specifications, design limitations, and guarantees. Sometimes a contract for the furnaces and their appurtenances is let first and the building and its appurtenant facilities are then designed to fit the furnaces to be furnished under the separate contract.

Definitions

A few definitions will help clarify the text of this paper. They are taken in large measure from a paper prepared by the author and his associates and read before the Conference on Incineration, Rubbish Disposal, and Air Pollution held by the Southern California Air Pollution Control Foundation, Pasadena, Calif., December 1954.

Refuse is the general term for the solid materials wasted by a community. It includes *garbage* (waste from the handling, preparation, and consumption of food), and *rubbish*. Rubbish is further divided into *combustible rubbish* (materials like paper, wood, rags, brush, and tree trimmings), and *noncombustible rubbish* (metals, glass, and the like). Such noncombustible rubbish as is delivered to an incinerating plant is removed from the furnaces as *ash* or *residue*.

The terms *fly ash* and *particulate matter* are used interchangeably to designate finely-divided solid particles in gases leaving an incinerator furnace. Such particles vary widely in size, but roughly may be divided into those which are large enough to be deposited on the ground after discharge from a chimney, and smaller particles remaining in suspension indefinitely.

The term *raw gas* is used to designate gaseous products of combustion as they leave the combustion chamber of the incinerator furnace, with their load of particulate matter. After these gases have passed through structures or equipment designed to remove particles of fly ash, we use the designation *treated gas*.

Particular definitions of refuse materials on the basis of laboratory analyses are rather limited in number. A relatively dry refuse might contain 20% of moisture, 20% of ash, and 60% of combustible matter. The combustible matter might contain materials given in Table II.

A refuse of these characteristics theoretically would require 3.68 lb. of air/lb. of refuse for combustion. The gaseous products of combustion (exclusive of ash) would amount to 6.32 lb. of air/lb. of refuse, with 50% of excess air.

Fundamental Considerations

Of fundamental consideration in design of a municipal incinerator is the responsibility of the designer and of the official representing the municipality, to

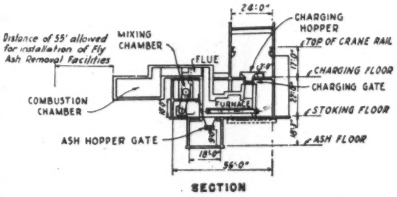

Fig. 3. Section of traveling grate furnace patterned after those designed and built in New York City and early ones designed and built for Baltimore and Pittsburgh. Refuse or rubbish has been delivered to the burning grate by an inclined traveling grate, as in New York City and at Providence, R. I.

TABLE II

Combustible Material

Material	Lb./Lb. of Combustible
Carbon	0.50
Hydrogen	0.06
Oxygen	0.40
Nitrogen	0.03
Sulphur	0.01
Total	1.00

the elected officials and to the general public. Such things as the following should be included:

(a) There should be a real local need. Incineration should have been selected as the method of disposal. The project should not be the result of a *sale*.

(b) Design of all parts should be carefully done with a view to efficient operation and economy so every expenditure will be needed.

(c) Adequate competition should be provided for special items of equipment and for general items by detailed plans and specifications.

(d) A reasonable future should be provided, with due regard to present expenditures.

(e) Future uncertainties and unknowns should be allowed for by leaving space in proper places for later installations.

Principal Parts of a Design

The design of an incinerator comprises the following principal parts:

(1) General aspects such as quantity and character of refuse, location of the plant and characteristics of the receiving airway. It is assumed such general parts will have been covered by an adequate engineering investigation and report.

(2) General arrangements, such as approaches, yard, scales, storage bin, building, clearances within the building, cranes, and ash-removal facilities.

(3) The part which comprises the furnaces and their appurtenances with bases of design for grate areas, volumes, dampers, flues, and of subsidence (or expansion) chambers, for removal of fly ash or particulate matter. This part constitutes structures and equipment which have to do with combustion.

(4) The chimney.

As already indicated, this paper is mainly directed to parts (3) and (4) of the foregoing items . . .

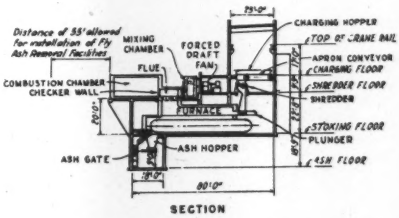

Fig. 4. A modification of the traveling grate. Pallets or plates are used for the grate. A plant of this sort has been in operation for some time at Englewood, N. J.

Bases of Design of Furnaces and Appurtenances

The first matter of importance in determining bases of design is the kind of refuse to be incinerated. As between mixed refuse (garbage and combustible rubbish) and rubbish, there are important differences, in particular as to the products of combustion and the amount of air required. These are illustrated in Table III.

Obviously, characteristics of the refuse affect most of the bases of design, but, because of the great variation in these characteristics, safe margins for limiting conditions are necessary.

The second matter to consider comprises capacity, size and the shape of the furnace. The principal bases of design are discussed in the following paragraphs. Bases given are applicable to combustion of mixed refuse and to an environment in which air pollution is not deemed to be highly critical:

(a) *Size.* Refuse incinerator furnaces have been built with rated capacities of 250 tons/24 hr. as in New York City, using moving grates. A more usual range is 100 to 150 tons.

(b) *Burning Rate.* Until recently a considerable number of refuse incinerators have been designed to operate at burning rates in excess of 70.0 lb./ft.^{2} of horizontal grate area/hr. These high rates of burning are considered to increase the quantity of particulate matter and other air pollutants. Lower burning rates are now considered to contribute to the control of the pollution of the receiving airways. A recent design for Evanston, Ill., has a burning rate of 53.5 lb./ft.^{2}/hr. for mixed garbage and rubbish.

(c) *Depth of Furnace.* Distances from the inside front wall to the rear wall or the diameter of a number of existing incinerators are given in Table IV. To facilitate stoking, an inside depth of not over about 10 ft. is indicated.

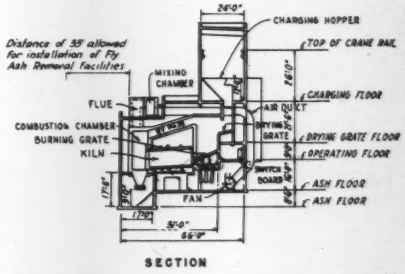

Fig. 5. Section of a grate and kiln furnace like one in operation at Atlanta, Ga. This is the only one of its kind in operation in this country. A number are operating in various European cities. A plant is now being constructed in Louisville, Ky. The section shown was developed for competitive bids at Los Angeles for a comparatively small unit having a rated capacity of 100 tons/24 hr.

TABLE III

Differences Between Types of Refuse

Item	Kind of Refuse	
	Rubbish	Mixed[a]
% moisture	15	54
Lb. of air/lb. of refuse for Combustion plus 50% excess	5.85	3.18
Cooling to 1600°F.	4.04	0
Total	9.89	3.18
Gaseous products of combustion in ft.³/lb. of refuse at 1600°F.	554	211

[a] 65% garbage at 75% moisture and 35% refuse at 15% moisture.

(d) *Volumes.* Table IV shows the unit vol. in ft.³/ton of rated capacity of furnaces, combustion chambers and subsidence chambers for a number of plants. It will depend considerably upon the characteristics of the refuse and should be larger for rubbish than for mixed refuse. For mixed refuse a furnace vol. of 12.5 and for rubbish of 20.0 ft.³/ton seems to be reasonable.

To meet air-pollution requirements, combustion and subsidence chambers, particularly the latter, have been much increased in unit volume of recent years. A vol. in these 2 structures of around 80 ft.³/ton is indicated.

(e) *Flues.* Area of flues is usually determined on the basis of limiting velocities in ft./sec. For the flue between the furnace and the combustion chamber, a relatively high velocity of 35 fps. or more is indicated to provide mixing and of other flues of 25 fps.

In the Los Angeles contract documents the contractor for the furnaces and equipment was required to guarantee the operation of the incinerator would meet requirements of the Los Angeles County Air Pollution Control District as regards discharges from the chimney top. This procedure required two things: (1) The contract drawings did not include any structure or equipment for air-pollution control, but a space was left of 55 ft. between the combustion chamber and furnace for these facilities. (2) Design limitations were stated in the contract documents to insure a reasonable and balanced design. These design limitations are shown in the Appendix.

Unit bases of design for a number of refuse incinerators are given in Table IV. Where a high removal of fly ash is desirable, rates of burning near 50 for rubbish and 60 for mixed refuse are indicated, both in lbs./ft.² of grate area/hr. A total unit volume for the furnace, the combustion chamber and the subsidence chamber approaching 100 for mixed refuse and somewhat over 100 for rubbish are indicated, both in ft.³/ton of rated capacity.

References in the ordinances to 50% excess air or to 12% CO_2 appear to class incineration of refuse with burning of uniform fuels like coal. The heterogeneous character of refuse, its low unit weight, its changing combustibility, and the relatively large quantity of cooling air make it difficult to approach a qauntity of 12% of CO_2.

A rational or realistic yardstick for regulating discharge from incinerator chimneys is much to be desired. Such a yardstick might limit the content of particulate matter in the gases entering the airway to a certain number of lbs./ton of refuse burned. Present available experience suggests a limit of 10 lb./ton, but much more data are needed before final determination. Yardsticks for other pollutants such as nitrogen and sulphur may be needed in some locations.

The inside depth of the furnace or of the burning grate is determined largely by ability to stoke and slice the fire. With mechanically moved grates, a depth of not over 10 ft. is desirable. Where unit bases of design are out of line, it is likely the rated capacity is too high. On account of outages of various kinds, experience indicates that real or net capacity is not over 90% of the rated.

Degree of Air-Pollution Control

Existing regulations relative to discharge of particulate matter from refuse incinerators were described in the Pasadena paper referred to above. A considerable number of municipal ordinances are in effect relative to this matter and most of them have taken one or the other of the following forms:

(a) The weight of particulate matter/1000 lb. of gas with 50% excess air; the usual limiting value being 0.85 lb. as established in the ASME model code.

(b) The weight of particulate matter/ft.³ of gas at standard conditions. The standard set up by the Los Angeles County Air Pollution Control District is 0.40 of a grain/ft.³ of gas at 60 F., 14.7 psia, and 12% CO_2.

None of the ordinances has undertaken to specify amounts of other substances in the gaseous products of combustion which may be tolerable as regards air pollution, such as oxides of nitrogen and sulphur. The 2 standards referred to above permit the amounts of particulate matter in chimney discharges given in Table V.

While little is known regarding quantity of particulate matter in raw gases, the amount is illustrated by the units of 15 lb./ton of mixed refuse and 20 lb./ton of rubbish. On this assumption, equipment to remove fly ash or particulate matter should have an efficiency based on the raw gases of upwards of 50%. To permit establishment of more accurate and realistic bases of design, full-scale tests are desirable to determine efficiency of existing fly-ash facilities of different kinds. As suggested in the Pasadena paper, such tests at Winnipeg, Washington, Milwaukee, and New York would provide information for 5 different kinds of incinerators.

Air-Pollution Control Facilities

Many bases of design of municipal refuse incinerators are scrutinized in the light of their effect on reduction of pollution of the receiving air. On this account, 3 general factors are important, as follows:

(a) A reduction in the quantity of under fire air.

(b) An avoidance of too frequent disturbance of the fire by charging refuse onto the grate.

TABLE IV

Background of Design Criteria Sizes of Furnaces and Appurtenances

Plant	Kind of refuse	Rate of burning in lb./ft.²/hr.	Vol. in ft.³/ton of rated capacity				Furnace inside depth or diam. ft.
			Furnace	Combustion chamber	Subsidence chamber	Total	
New York City							
Betts Avenue	M	69.5	25.0	15.7	40.0	80.7	8.0
Gansevoort	M	64.0	16.0	28.0	40.0	84.0	8.0
Washington—No. 3	R	51.0	14.3	29.0	204.0	247.3	8.5
Baltimore	M	57.5	11.1	16.5	11.0	38.6	8.75
Brookline, Mass.	M	98.5	9.1	25.7	11.4	46.2	
Cincinnati—No. 3	M	108.6	7.24	20.0	93.6	120.8	11.08[a]
Milwaukee							
Green Bay	M	84.2	12.3	18.3	10.5	41.1	11.75[a]
South Side	M	56.8	12.4	16.4	37.3	68.1	11.00
Winnipeg	M	78.0	9.0	16.0	18.8	43.8	11.72[a]
St. Louis							
South Side	R	50.0	14.5	31.8	57.0	103.0	7.5
Evanston	M	53.5	13.6	28.3	53.0	95.0	10.0

Volumes are exclusive of flues.

[a] Diam of round furnace.

TABLE V

Particulate Matter in Chimney Discharge
Pound of Fly Ash Permitted/Tons of Refuse

% moisture in refuse	Wet refuse (At 0.85 lb./1000 lb. of gas)	Dry Solids (At 0.85 lb./1000 lb. of gas)	Wet refuse (At 0.40 gr./ft.³)	Dry solids (At 0.40 gr./ft.³)
20	10.7	13.4	8.9	11.1
30	9.6	13.7	7.8	11.1
50	7.4	14.7	5.6	11.2

(c) A lower burning rate.

Specific yardsticks or procedures in relation to the above are not, as yet, fully developed.

In a study of air-pollution control facilities, 3 general characteristics should be kept in mind, as follows:

(d) Facilities which can be used with hot gases of combustion.

(e) Facilities requiring cooled gases of combustion.

(f) Facilities using water.

There are many devices for removing fly ash or particulate matter from gaseous products of combustion. Some have been designed by public and private practicing engineers, others by manufacturers. None removes true gases, such as oxidized nitrogen and sulphur, except water sprays should remove soluble SO_2. The various devices in use or advocated are illustrated by the following list:

(g) Subsidence chambers with various kinds of trapping and impingement walls and corners. This device is applicable to hot gases and is extensively used.

(h) Subsidence chambers with water sprays and a bath as installed at Milwaukee, Miami, Philadelphia, and, without a water bath, at a number of rubbish incinerators in the Los Angeles area.

(i) Cyclone or centrifugal precipitators made in different forms by a number of manufacturers. All require the gases to be cooled to about 700 F. Few have been installed in refuse incinerators. Cyclones are used in the Hempstead, L. I., incinerator on gases which have passed through waste-heat boilers.

(j) Bag filters made of steel or glass mesh. These require cooled gases. None has been installed in refuse incinerators.

(k) Electrostatic precipitators which are used in power plants on gases cooled by passing through a boiler. None has been installed in refuse incinerators.

(l) The municipal refuse incinerator at Framingham, Mass., is equipped with a scrubber for the gaseous products of combustion. Induced draft is used and raw gases are drawn through a scrubber 12.5 ft. diam. and 17.5 ft. high, with a hopper at the bottom and a discharge into a pool or tank of water. Results of operation are not yet available.

Ten years ago the author made a report on the control of fly ash to the District of Columbia. At that time the following methods of fly-ash control and removal were considered: dilution and dispersion, sedimentation and trapping, cylcones, water, filters, electrical precipitation.

Samples of fly ash were obtained, as removed by electrical precipitation, by cylcones, by gravity filters of the Lynch type, and by subsidence. The results are shown on Fig. 6. Illustrative costs of equipment for one furnace unit having a rated capacity of 125 tons were prepared (Table VI).

It was concluded adequate sedimentation and trapping chambers should be installed, with the following comment:

Because of no clear and specific yardsticks relating to chimney discharges and to possible resulting nuisances, and because there is no simple and inexpensive equipment with applicable experience, the necessity for a further removal of fly ash is difficult of (present) determination.

There is not enough precise operating information to permit classification of the foregoing as to efficiency and other qualities. Having in mind the present limited data as to what might be accomplished by these various devices for removing fly ash from refuse incinerator gases, it is easier to suggest what not to do than to arrive at a selection for a particular local condition. Considering public money should be spent only for *sure things*, any device other than subsidence coupled with baffling, trapping and impingement, cannot be recommended.

Fig. 7 shows the subsidence chamber planned in 1945 for Washington, D. C.

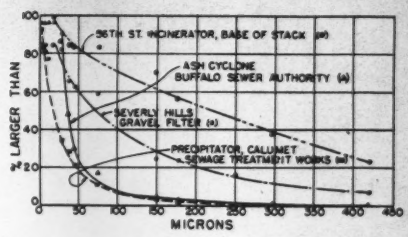
% LARGER THAN
MICRONS
96TH ST. INCINERATOR, BASE OF STACK (m)
ASH CYCLONE BUFFALO SEWER AUTHORITY (s)
BEVERLY HILLS GRAVEL FILTER (s)
PRECIPITATOR, CALUMET SEWAGE TREATMENT WORKS (m)

Fig. 6. Sieve analysis of fly ash removed by various methods.

TABLE VI

Fly-Ash Removal Equipment Costs

Method	Installation Cost 1946	Installation Cost 1956
Cyclones	$20,000	$ 40,000
Gravel filters	35,000	70,000
Water	25,000	50,000
Electrical precipitation	60,000	120.000

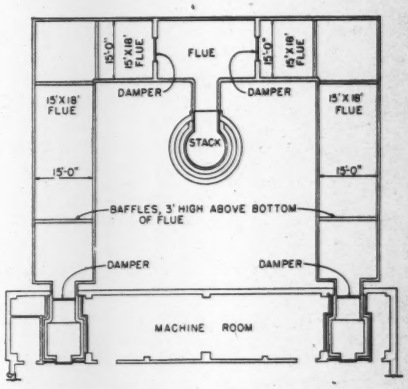

Fig. 7. Subsidence chamber planned for Washington, D. C., 1945.

TABLE VII

Data from Gansevoort Rubbish Plant

Plant	Kind of refuse	Lb./ton of refuse: Particulate matter in raw gases	Lb./ton of refuse: Fly ash removed	% removed
New York	Mixed	15	5	33
Washington	Rubbish	20	14	70

TABLE VIII

Air needed for Combustion

Item	A—Lb. of air/lb. of refuse	
% moisture	15	54
Air required for combustion	3.90	2.12
Excess at 50%	1.95	1.06
To cool gaseous products of combustion to 1600	4.04	0
Total air	9.89	3.18
Moisture in refuse	0.15	0.54
Combustible	0.64	0.35
Total	10.68	4.07

Item	B—Fan capacity in ft.³/lb. of refuse	
% moisture	15	54
Natural or forced draft at 70 F	132	42
350 F	202	65
Induced draft at 700 F	313	119

It has a vol., as built, of 204.0 ft.^{3}/ton (Table IV). There are 2 chambers, each having 3 baffles or impingement walls. The baffling can be changed and water treatment added later if desired. It should be noted the Battelle Memorial Institute has made tests on large models of different baffle arrangements for New York City. It is hoped results will be published.

Little is known about removal efficiency of subsidence chambers or other devices. The author has been given informal data for the Gansevoort plant burning mixed refuse, in New York City, and the new plant in Washington, burning rubbish. Results are summarized in Table VII.

Assuming a chimney discharge of under 10 lb./ton of refuse as charged is tolerable (preceding), under some present smoke ordinances, the foregoing efficiencies are sufficient.

When adequate subsidence chambers are installed, there is a problem of removing fly ash deposited on the bottom by gravity, by trapping, and by impingement. We have found a vacuum-cleaning system for removing the deposited material works well and improves efficiency of the subsidence chamber.

Such a vacuum-cleaning system is specified to handle fly ash at temperatures up to 1000°F. For a furnace unit having a rated capacity of 100 tons/24 hr., it is found the vacuum-producing unit should have a capacity of about 500 cfm. of air at a suction of 10.3 in. of mercury and of 1300 cfm. at a suction of 8.4 in. of mercury.

The vacuum-cleaning system can be made to discharge to primary and secondary dust separators of the centrifugal and of the bag type, respectively. Purpose of the separators is to provide some storage and to release and collect fly ash from the vacuum system for disposal or use.

Draft Facilities

The air needed for combustion is provided by forced draft, by induced draft or by natural draft. The first two require fans and the third a chimney of adequate height and cross-sectional area. With induced draft, the chimney can be relatively small. With natural draft, it should be large enough to draw gaseous products of combustion through the grate and away from the furnace chamber. With forced draft, the suction need only operate from over the grate. Dampers are required to control natural draft.

The quantity of air needed for combustion is illustrated in Table VIII.

The quantity is larger for induced draft because the fan must handle moisture and volatile matter from refuse in addition to air for combustion, and gaseous products of combustion must be reduced constantly in temperature to not over 700°F.

Because characteristics of refuse are so variable and conditions of incineration change so much from day to day, fans should have variable-speed drives to provide a range in capacity from the rated to 20% of the rated capacity. Sometimes preheated air is provided (for rainy weather) requiring a fan of larger capacity. Thus, for 100 tons of refuse, a fan with a capacity from about 5000 to about 25,000 cfm. would be installed.

Forced draft with an adequate chimney is a satisfactory design procedure. For many environments, a chimney 150 to 175 ft. high is adequate. It should have an area at the top of about 0.25 ft.^{2}/ton of rated capacity . . .

Looking to the Future

In the author's opinion, the present time may be characterized as one of transition. The design of municipal refuse incinerators is being considerably affected by public interest and by changing habits of people as regards purchase and use of packaged goods, increased practice of wrapping garbage, greater use of garbage grinders, and the consequent change in refuse characteristics. It is suggested there is not enough information to permit a realistic appraisal of the extent and kind of facilities for treatment of raw gases of combustion. Thus, realistic bases of design and expenditures cannot be stated.

The new characteristics of refuse apparently have become somewhat stable, although an increase in garbage grinding may occur.

Looking to the future, it is desirable all aspects of the air-pollution problem should be explored, including field tests and operating records.

TABLE IX

Cost Breakdown

Part		Approximate % of total cost
(a)	Scales, yard, storage bin and outside appurtenances	11.0
(b)	Building and cranes	37.0
(c)	Furnaces, combustion chambers, flues and appurtenances	35.0
(d)	Relatively simple fly ash removal facilities	7.0
(e)	Chimney	10.0
	Total	100.0

Summary Statement

Ample operating experience permits sound bases of design to accomplish satisfactory results with good economy and ample competition, except in some aspects of facilities to reduce air pollution. In this part there is not as yet a sufficient amount of operating data to permit a realistic adjustment of costs and results in operation to the needs of the receiving airway. Therefore, simpler and less costly facilities arranged for later additions, if needed, are recommended. Present experience suggests subsidence chambers can be designed to avoid undesirable air pollution. There is no ground to assert that municipal refuse incinerators should not be built because of inability to operate without undue air pollution.

In summary, it is helpful to consider the design criteria with respect to several parts of the design (Table IX).

It is surprising how poor designs have been made for items (a) and (b) of Table IX, amounting to some 48.0% of the expenditure. Designs for item (c) have occasionally suffered by pressure of competition under guarantees which would not be met in routine operation. While simple fly ash-removal facilities are not a large part of construction cost, more complicated facilities at a greater first cost are likely to increase the annual cost in a greater proportion.

A competent engineering investigation should first be made to determine the method of disposal best suited to the local conditions. If refuse incineration is adopted, bases of design and plans and specifications should be made so as to conform to a competent and realistic appraisal of the operation of the plant. Reasonable flexibility should be included to provide for future changed conditions.

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Design Criteria for Municipal Incinerators—The Customer's View*

ABRAHAM MICHAELS
City of Philadelphia

This paper originally included more information. It has been excerpted for the Journal and includes those parts of direct interest to air pollution and its control. —Editor

What is refuse? A typical dictionary definition of refuse is "that which is discarded as worthless or useless."

In 1941, the American Public Works Association published a book entitled "Refuse Collection Practice" containing a table classifying refuse materials (Table I).[1] This table is still used as a definition of refuse. However, this paper will be confined to the following three basic categories; garbage, combustible refuse, and non-combustible refuse.

Garbage. Organic residue of both animal and vegetable matter resulting from preparation and consumption of food.

Combustible Refuse. Material which can be incinerated including furniture, oil cloth, paper and paper products, rags, shrubbery, wood, and wearing apparel.

Noncombustible Refuse. Material that cannot be incinerated including ashes, glass, cans, dirt from floor sweepings, masonry, and metals.

Although municipal refuse disposal concerns itself with all of the materials shown in Table I, materials to be handled by an incinerator usually consist of combinations of garbage, combustible refuse, and noncombustible refuse depending upon other factors which will be discussed later in the paper. In any event, it is obvious incinerators must handle a variety of materials.

Refuse-Disposal Methods

Recognition of other refuse-disposal methods is important if a thorough understanding of incineration is to be realized. So, briefly, other methods are herein described.

Probably the oldest methods of garbage disposal are composting and animal feeding. Farmers for thousands of years have been composting food wastes, human and animal excrement, and vegetation in compost heaps and used the organic humus produced to enrich soil. Until recently, there has been virtually no change in the compost process. However, studies of sanitary, scientific composting methods have been under way for a number of years, and it appears this may become an important method of refuse disposal. Hog feeding of garbage has been practiced for hundreds of years. A newly-discovered animal disease called vesicular exanthema threatened to eliminate this method of disposal until it was determined that disease could be controlled by precooking garbage. There is still some question about the economic practicability of cooking; therefore, developments in this field might conceivably have a tremendous effect upon incinerator design in various communities.

Another method of garbage disposal, now virtually obsolete, is garbage reduction, a process in which grease is extracted from garbage and sold. Residue or tankage produced from this process was once usable as a weak organic fertilizer, but since the advent of chemical fertilizers, market for this material has nearly vanished and the tankage itself presents a disposal problem.

The oldest method of disposing of combustible waste, with or without garbage, is open dump burning, a method by today's sanitation standards considered unacceptable. Recognizing the need for sanitary refuse-disposal methods, municipalities are studying and installing incinerators, sanitary fills and garbage grinders. The sanitary-fill method of disposal consists of dumping refuse on the ground or in a trench, compacting the refuse by driving a bulldozer or other heavy piece of equipment over it, and covering the refuse with a layer of earth to prevent rodents and insects from getting in and odors from getting out. A properly-operated sanitary fill is an excellent method of disposal for small communities with ample waste land available at an economical hauling distance from the bulk of the population. Home garbage grinders are a good sanitary means of disposing of garbage, but they do not assist in the problem of disposing of other combustible waste.

Considering all disposal methods described, and considering growth of urban metropolitan areas, it appears the best present-day sanitary method of disposing of refuse is incineration. Having reached this conclusion, let us explore factors to be considered in establishing incinerator-design criteria.

Factors Governing Incinerator-Design Criteria

First one must know the quantity of material to be disposed of. This could be difficult since most municipalities not operating incinerators have little need for weight and/or volume records. Assuming figures are not available, estimates could be made by actually surveying collections, by comparing the subject municipality with a municipality of comparable size, or by using accepted average refuse-production figures if such figures are available. Since a true average has never been established, the American Public Works Association, through its Committee on Refuse Disposal, is currently starting a nation-wide survey to determine an average. This survey will attempt to consider important variables such as season, location, and community standard of living, and provide information which municipalities of all types will be able to use in estimating refuse-disposal requirements. However, one must recognize these results will not remain firm for long. Radical changes in the nation's living habits over the past 2 decades are producing large increases in the quantities of paper being used and slight decreases in the amount of garbage produced in the home. In less than 20 yr. the average daily production of refuse will probably have increased to somewhere between 4 and 6 lb./capita.

The next important factor is refuse-collection practices of the municipality since this will determine types of materials, specific weights, per cent of moisture, and proportion of organic, com-

[1] *Refuse Collection Practice.* Committee on Refuse Collection and Disposal, American Public Works Association, Chicago, Ill. p. 17 (1941).

* Excerpts from a paper presented at the ASME semi-annual meeting, Cleveland, O., June 17-21, 1956.

bustible and noncombustible materials handled. For convenience of the taxpayer, most municipalities would prefer to pick up all refuse at one time, but this type of collection is not always practical. For instance, where hog farmers collect garbage for feeding, the householder is asked to separate garbage from the rest of the refuse, and to reduce collection and disposal costs, some municipalities separate ashes, tin cans and bottles from combustible waste. The type of collection vehicle is also a factor in designing an incinerator. The density of combustible refuse without garbage could vary from less than 200 lb./yd.^{3} for open-truck collections to over 300 lb./yd.^{3} if compactor-type trucks are used. This obviously would have an effect on the design of a storage pit and crane. Again, in connection with storage-pit design, one would be interested in the municipality's practices concerning holiday collections, Saturday and Sunday operations, the daily collection schedules of city forces, and schedules of private collectors who might be hired to collect refuse from commercial and industrial establishments.

Another important consideration is the plant site. Its location with respect to the theoretical center of collection is important from the over-all refuse collection and disposal standpoint since, generally speaking, the cost of collecting refuse represents 75 to 80% of the over-all cost of collection and disposal. Proximity to the ultimate disposal site must be considered, and proximity to residential areas, present and future, will also affect the over-all design of the plant. And from an air-pollution standpoint, even the study of prevailing wind directions would provide valuable information to the designer.

Speaking of air pollution, all large municipalities and many smaller ones are becoming aware of the need for proper air-pollution controls. Incinerators must be designed to meet municipal air-pollution regulations. Municipalities having such regulations today base their limits of acceptable stack emissions upon boiler operations. For instance, many cities use stack-emission limits of 0.85 lb./thousand lbs. of gases corrected to 12% CO_2. Unlike a boiler, a municipal incinerator operates most efficiently with 100% or more excess air, resulting in stack CO_2 readings of between 3 and 6%. Assuming then the ASME considers municipal incineration a related field, attention should be given to a more realistic definition of acceptable stack effluent from incinerators. Probably a relationship between tonnage incinerated on a dry basis and total weight of stack particulate matter would be more realistic.

Getting back to factors governing design criteria, other nuisance factors such as noise, odor and over-all aesthetic appearance of the plant must be included . . .

Another factor in establishing design criteria is extent of mechanization and automation desired by the municipality. These phases of refuse incineration have only recently been receiving attention by designers. Good design can improve present operating standards. However, one must not lose sight of the type of material handled which tends to resist mechanization and automation. In considering this aspect of design, one also must consider the availability of technically qualified personnel to operate and maintain a complex installation, as compared to the availability of unskilled labor required to operate a basically manual plant. The city of Philadelphia, at the present time, has a rather large unskilled labor force and must consider this factor when designing incinerators.

Finally, as is true in designing any industrial installation, the cost and availability of power, water and sewage facilities should be considered. This is particularly important if a wet type of fly-ash eliminator is to be included in the plant.

TABLE I
Classification of Refuse Materials

	Class	Description		Origin	Disposition
Refuse	Garbage	Wastes from the preparation cooking, and consumption of food Market refuse, waste from the handling, storage, and sale of produce			
	Rubbish	Combustible rubbish	Paper Cartons, boxes, barrels Wood and excelsior Tree branches Yard trimmings Wood furniture Bedding	From homes, hotels, institutions, stores, markets, etc.	Municipal responsibility for collection and disposal
		Non-combustible rubbish	Metals Tin cans Metal furniture Dirt Glass Crockery Other mineral refuse		
	Ashes	Residue from fires used for cooking and for heating buildings			
	Street Refuse	Street sweepings Dirt Leaves Catch basin dirt Contents of litter receptacles		From streets, sidewalks, alleys, vacant lots, etc.	
	Dead Animals	Small animals: cats, dogs, etc. Large animals: horses, cows, etc.			
	Abandoned Automobiles				
	Industrial Refuse	Solid waste resulting from industrial processes and manufacturing operations, such as: food-processing wastes, boiler house cinders, lumber scraps and shavings, metal scraps and shavings, etc.		From factories, power plants, etc.	Private responsibility for disposal

Refuse Collection Practice, Committee on Refuse Collection and Disposal, American Public Works Association, Chicago. (1941) p. 17.

Description of Current Installations

There are many different types of incinerators operating in the country today. Most of them can be classified as floor-dump or bin-and-crane types. A floor-dump incinerator is one in which material is dumped from the collection vehicle to a floor, then pushed by hand or tractor into an opening over the furnace. The bin-and-crane plant, as the name implies, consists of storage bin and one or more overhead materials-handling

cranes. In this type of installation, the truck dumps the material into a storage bin and the crane hoists a bucketful of material at a time from the storage bin dumping it into the furnace through a charging opening.

There are several different types of refuse furnaces presently in operation. The most common are the following:

(a) *The single-chamber, cylindrical, batch type.* This is a refractory-lined furnace charged through a door in the ceiling. A batch of material is dropped into the furnace and allowed to burn itself down after which residue is dumped from the furnace. This furnace generally contains a rotating cone with extended rabble arms designed to effect continuous stoking thereby reducing the amount of required manual labor.

(b) *The single-or multiple-cell, rectangular, batch type.* This may be refractory lined or water cooled with a charging door in the ceiling located over each cell either centrally or near the back end of the furnace; the grates could be either fixed or of a multiple-rocker-arm design set level or inclined.

(c) *The single-or multiple-cell rectangular continuous-feed type.* This may be refractory lined or water cooled. Charging of the furnace can be by a gravity-fed chute at one end of the chain grate or by a charging conveyor fed by a gravity chute.

(d) *The inclined rotating-kiln type.* This consists of a refractory-lined continuous-fed inclined cylinder which moves and stokes the refuse by rotating in an inclined position.

In virtually all cases, with the possible exception of the rotating kiln, a certain amount of manual stoking is required. Generally, furnaces are lined with refractories. This is essential in the batch-feed single-cell furnace in order to retain heat necessary to start ignition when a new batch of material is inserted. Water-cooled walls have been used in furnaces in both the multiple-cell batch-feed furnace and the chain-grate-stoked furnace. The high amount of combustible refuse and the ever-decreasing amount of garbage in municipal refuse has virtually eliminated the need for using auxiliary fuel except where only garbage is incinerated, or during periods of wet weather. On the other hand, the increasing Btu. value of the refuse makes it essential additional air be introduced to keep temperatures down. A well-operated furnace should operate at temperatures between a low of 1200 and a high of 2000 F. with an average of 1700 to 1800 F. The 1200 minimum temperature is desirable because at this temperature all odor-producing hydrocarbons will have been incinerated, thereby eliminating a potential air-pollution nuisance. A high of 2000°. is desirable because the type of refractories currently used in incinerators deteriorate rapidly at temperatures over 2000 F. and the higher gas velocities produced by temperatures in excess of 2000 F. reduce the effectiveness of fly-ash trapping devices, since the particulate matter moves at higher speeds tending therefore to escape fly-ash traps.

Recently a number of new ideas have been developed to reduce labor and other incinerator operating costs. However, since municipal officials cannot afford to *speculate*, progress in this field has been slow.

As mentioned earlier, the problem of air pollution is becoming more acute and municipalities are insisting upon fly-ash control devices in municipal incinerators. Since the prime purpose of a municipal incinerator is to dispose of refuse and not to utilize all of the available Btu., gas temperatures are usually around 1000 F. when they enter the incinerator stack. These high temperatures limit the type of fly-ash removal installations and make it difficult or expensive to use eliminators common to boiler plants. The 3 principal types of devices now used are: (a) large settling chambers in which gas velocities theoretically are reduced to allow the particulate matter to settle, (b) wet scrubbers, and (c) dry fly-ash traps in which the design attempts to deflect the flow of gases in a manner which will cause the particulate matter to be trapped by strategically located structures . . .

Construction and Operating Costs

The customer is interested in his construction and operating costs; however, municipalities often view this problem somewhat differently than does private industry. Municipalities are generally confronted with the need to borrow money for a capital improvement such as an incinerator; at the same time that they are faced with the additional operating cost of a new plant. The tendency on the part of a municipality is to attempt to keep initial cost as low as possible since the administration making the improvement may not even be around to pay the operating bills by the time the plant is completed. It is therefore incumbent upon the engineer to present the operating-versus capital-cost facts to the municipality so that, even though the municipality might decide to build the cheapest plant, at least the engineer has apprised the customer of the advantages and disadvantages of high initial cost. There is a great difference in construction costs, varying from a low of less than $1000/ton for incinerators without automation or mechanization or air-pollution control devices to a high of approximately $5000/ton for a well-designed plant containing all of the foregoing desirable features for providing an installation which will keep operating costs to a minimum. Table II contains recent data on incinerator construction costs.[2]

Determining typical operating costs is rather difficult because some municipalities include the cost of removing residue; others exclude maintenance costs, etc. However, a plant containing an average amount of mechanization, operating on a 24 hr. a day basis, and having a minimum capacity of 300 tons/day, if efficiently run, should cost between ½ and 1 manhour/ton to operate. Obviously, the type of material handled, *i.e.*, mixed refuse, garbage, rubbish *etc.*, the degree of mechanization, the air pollution and other health standards to be met, and the housekeeping standards all have a bearing upon the ultimate operating costs. The customer should be aware of these factors and should be able to advise the consulting engineer of the standards he requires.

The Consulting Engineer's Function

In conclusion, what does the customer expect of the consulting engineer? First and foremost the customer wants a plant that works. Incinerators that fail to operate are not uncommon. An outstanding example of such a failure is the Lacy Street plant in Los Angeles built in the late 1940's for $1,000,000. After several years and many costly changes, this plant has finally been made to work. Next, the customer wants a plant that will operate at full capacity with as little breakdown and maintenance as possible. A trouble-free incinerator has not yet and may never be built. As a matter of fact, to provide ample time for relining furnaces (every 3 to 5 yr. for firebrick walls of superduty quality), repairing and/or relining combustion chambers and flues, repairing broken crane cables

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[2] Prepared by W. A. Xanten, Superintendent, Division of Sanitation, Washington, D. C.

City and State	Plant Designation	Capacity tons/24 hr.	Yr. Completed 19....	Material Burned	Type of Grate	No. of Furnaces	Capacity of Each Furnace	Combustion Chamber Total	Type of Dust Collection System
Atlanta, Ga.	City of Atlanta Incinerator	700	'50	[b]Refuse	Rotary Kiln Reciprocating Grate	4	175	4	Settlement
Baltimore, Md.	No. 4 Incinerator	800	'55	Refuse	Hydraulic Stoker	4	200	4	Baffle & Checker Wall
Brookline, Mass.	Brookline Incinerator	300	'52	Refuse	Monohearth	2	150	2	Baffles & Screens
Buffalo, N. Y.	Westside Incinerator	400	'53	Garbage	Cast Iron	3	133	3	Baffles & Screens
Cincinnati, O.	Westfork Incinerator	500	'54	Refuse		4	125	4	Expansion Chamber
Cleveland, O.	— — —	900	'35	Refuse	Hydraulic Stoker[c]	6	150	—	Expansion Chamber
Fort Worth, Tex.	Valley View	250	'53	Refuse	Tilted	2	125	1	Settlement
Hartford, Conn.	North Meadows Municipal	600	'54	Refuse	Circular, Manual Dump	4	150	4	Expansion Chamber
Jacksonville, Fla.	Margaret St. & McCoy Blvd.	300	'52	Refuse	Cast Iron	2	150	2	Settlement
Los Angeles, Calif.	Gaffey Street	100	'54	Rubbish	Morbo-Stoker	1	100	1	Settlement
Los Angeles, Calif.	Lacy Street	400	'55	Rubbish	Suspended Water Cooled	2	200	2	Water Spray
Miami, Fla.	20th St. Incinerator	900	'55	Refuse	Monohearth	6	150	6	Water Spray
Milwaukee, Wis.	Lincoln Ave. Plant	300	'55	Refuse	Inclined	2	150	2	Water Spray
Milwaukee, Wis.	Green Bay Ave. Plant	300	'54	Refuse	Monohearth	2	150	2	Water Sprays & Baffles
Minneapolis, Minn.	South Side Incinerator	300	'39	Garbage	Shaker type Finger and Dump Grate	3	100	3	Settlement
New Orleans, La.	Incinerator B	200	'29	Refuse	Stationary Bars	2	100	2	Settlement
New Orleans, La.	Incinerator C	200	'29	Refuse	Stationary Bars	2	100	2	Settlement
New York City, N. Y.	South Side Incinerator	1000	'54	Refuse	Traveling Grate	4	250	4	Expansion Chamber
Norfolk, Va.	— — —	400	'45	Garbage	Cast Iron Herringbone	4	100	4	Settlement
Philadelphia, Pa.	Southeast	300	'51	Rubbish	Monohearth	3	100	3	Settlement
Rochester, N. Y.	West Side	450	'55	Refuse	Monohearth	3	150	3	Water Sprays & Baffles
Rochester, N. Y.	East Side	600	'56	Refuse	Monohearth	4	150	4	Water Sprays & Baffles
Toronto, Ont.	Commissioners Street Plant	900	'55	Refuse	Monohearth	6	150	6	Settlement & Baffles
Washington, D. C.	Mt. Olivet Incinerator	500	'55	Rubbish	Inclined Hydraulic	4	125	4	Expansion Chamber
Winnepeg, Man.	— — —	400	'48	Refuse	Monohearth	4	100	4	Settlement

[a] Prepared by William A. Xanten, Superintendent, Division of Sanitation, Washington, D. C.
[b] Mixed Refuse
[c] Converted 1955
[d] Hours per week
[e] Cost of both plants

and burned-out electrical crane parts, furnace charging, stoking and discharging mechanisms, clogged drains, *etc.*, an incinerator could be down for as much as 20% of its life. However, when the plant is operating, it should do so at full capacity with relatively few breakdowns. The engineer is expected to design a nuisance-free plant which will meet all city regulations and which will be a good neighbor.

There are 2 approaches to designing a plant. The first is to open bidding to all types of incinerator manufacturers by establishing loose specifications defining the size of the plant in tons of capacity, maximum and minimum operating temperatures, minimum furnace grate areas, minimum furnace vol., minimum combustion chamber vol., maximum gas velocities in flues and combustion chamber, sizes and types of forced-and-induced-draft fans, methods, if any, of providing over-fire air, the refuse to be handled, the condition of the residue, *i.e.*, % of combustible or organic material remaining after incineration, and the municipal regulations to be met, *i.e.*, air-pollution regulations, environmental sanitation regulations, *etc.* In accepting this type bid, the engineer must receive some data from the bidders to use in evaluating the bid. He should be specifically interested in the number of manhours required to operate the plant, water-and power-consumption figures, life of the various components, and experience record of the manufacturer. An evaluation of bids must consider all factors. After choosing the manufacturer of the furnaces and appurtenances, the engineer designs the incinerator structure around equipment to be supplied by the successful equipment bidder.

The other method of designing a plant is to determine the type and size of furnaces and appurtenances during the preliminary-study stage and design the equipment and plant structure simultaneously. In the first method the manufacturer can be held to a capacity guarantee; in the second the equipment manufacturer is not responsible for meeting over-all plant capacities. Since incinerator design is still in its infancy, and since municipalities would have great difficulty in obtaining funds for experimental work in the incinerator field, I believe the first method of preparing specifications for bids is more desirable at this time.

CONSTRUCTION COSTS[a]

STACKS			TYPE OF WALL CONSTRUCTION						WASTE HEAT UTILIZATION					PLANT OPERATION		COST OF PLANT IN $1000 UNITS		
			FURNACE		COMBUSTION CHAMBER		FLUE											
Number	Height ft.	Diameter ft.	Solid	Suspended	Solid	Suspended	Solid	Suspended	Power Generation	Number of Boilers	Horsepower	Pressure, psi	Steam lb./hr.	hr./day	days/wk.	Incinerator	Building	Total
2	—	8	x		x		Steel		No	4	—	175	32,000	24	7	—	—	1850
2	150	12	x		x		x		No	None				24	6	695	1498	2153
1	170	10.5	x		x		x		No	None				8	5	204	657	861
1	185	12.5		x	x		x		No	None				16	5	500	1000	1500
2	175	10	x		x		x		No	None				24	5	514	980	1494
3	175	—	—	—	—	—	—	—	No	None				24	7	—	—	875
1	125	8.5	x		x		—		No	None				20	6	372	—	—
2	180	22.75	x		x		x		No	None				16	—	1070	364	1434
1	109	—	x		x		x		No	None				80[d]	6	—	—	602
1	175	8		x		x		x	No	None				—	—	156	358	514
1	175	10	x		x		x		No	None				—	—	400	300	700
2	150	12	x		x		x		Yes	4	—	250	26,000	24	7	—	—	3300
1	175	10	x		x		x		No	2	200	—	—	8	5	244	743	987
1	175	10	x		x		x		No	2	150	—	—	16	5	249	676	925
1	180	8		x	—	—	x		No	None				16	5	—	—	275
2	125	5.5	x		x		x		No	None				14	6	300[e]	230[e]	530[e]
2	125	5.5	x		x		x		No	None				20	6	See note below		
2	200	11		x		x		x	No	1	—	High	—	24	6	2460	2350	4810
2	100	—	x		x		x		No	None				9	6	—	—	275
1	166	11	x		x		x		No	None				24	5⅔	—	—	1330
1	165	13		x		x		x	No	None				16	6	460	940	1400
2	204	13		x		x		x	No	None				16	6	640	1470	2110
3	175	—	x		x		x		No	None				16	5	880	1015	1895
2	166	11		x		x		x	No	None				24	5	—	—	1971
1	175	12.5	x		x		x		No	None				24	5	341	522	863

Frankly, there are very few consulting engineers in the country today who have sufficient incinerator-design experience to do a good job. Since demand for incinerators is rapidly expanding, and since incinerator design is similar to power-plant design, it is my belief mechanical engineers should explore municipal incineration thoroughly so they might be in a better position to aid municipalities in solving problems in this field.

Industry's Function

On the other hand, industry has an equally important obligation. Many improvements in the field of incineration have been made by industry; however, until recently the demand has been too small to warrant expenditures of appreciable sums of money for research. This condition has changed and is continuing to change to the extent that the industries most closely related to incineration, specifically, the boiler industry and materials handling and process industries, should reexamine the municipal incineration field with a view toward radically changing and improving such functions as furnace charging and stoking, residue handling and fly-ash elimination.

Some individuals and companies have recently taken the initiative and have come up with ideas and designs which differ radically from existing types of incinerators. Some of these will meet the test; others will fail. The important thing is that the field is ripe for improvement and great strides should be made within the next decade.

The AEC Fallout Monitoring Network*†

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The Health and Safety Laboratory of the U. S. Atomic Energy Commission has measured radioactive fallout in the United States since 1951 when the weapons testing programs at Eniwetok Atoll was augmented by the establishment of a continental test site in Nevada.

With assistance and cooperation of the U. S. Weather Bureau, the Commission set up a network of monitoring stations comprised of 89 stations when tests are conducted in Nevada. Other times the number is reduced to 41, a sufficient number of sampling sites for more uniformly diffused radioactive debris that may originate from detonations beyond continental limits.

The Basic Mechanics of Fallout

The intense heat accompanying detonation of a nuclear device volatilizes the radioactive fission products as well as the various components of the test assembly. This mass of luminescent gas, forming the fireball, sucks up varying amounts of dust, initially nonradioactive, from the ground by convection. A portion of the convected material may reach the fireball and vaporize. Inert dust sucked into the fireball in the advanced stages of cooling may serve as nuclei on which the fireball vapors condense as a radioactive coating. Some of the vapors will condense around ionic nuclei and form discrete fume particles which may or may not aggregate with larger particles of inactive dust.

The enormous amount of radioactivity (8.2×10^{11} curies gamma-activity 1 min. after detonation of a weapon equivalent to 20 kilotons of TNT) decays rapidly, and at any subsequent time the activity can be approximated by the relationship $A = A_1 t^{-1.2}$ where A_1 is the activity at one unit of time after the detonation. As a rule of thumb, radioactivity will decrease 10-fold for every 7-fold increase in time since the detonation.

The dispersion of radioactive particulates within the cloud is characterized initially by a wide range of particle size. Particles from less than 1 μ to about 10 μ in diam. are likely to be discrete spheres, whereas larger particles are more apt to consist of fission products condensed on dust convected from the ground. Included in this portion of the dust are particles of relatively large diameter often greater than 100 μ.

The radioactive particles form at great heights above the ground. As they begin their descent to earth, they are carried cross country on a path that depends on the wind patterns. The manner in which a particle descends through various layers of the atmosphere, each characterized by its individual turbulent properties, is not well understood.

A 100 μ particle, assuming a density of 3, settles by gravity at a terminal velocity of 180 ft./min.; hence sedimentation may play a dominant role in descent of the relatively large particles. However, a 1 μ particle of the same density will settle at approximately .02 ft./min.—a rate of fall not sufficient to explain the rapidity with which such particles sometimes do reach the ground.

TABLE I

Principal Isotopes Present at Various Times Following Fission

Isotope	at/wk.	at/mo.	at/yr.
Sr^{89}	2.1	6.4	2.6
Sr^{90}	—	—	1.9
Y^{90}	—	—	1.9
$_2Y^{91}$	2.4	7.2	4.0
Zr^{95}	2.4	7.6	7.0
$_2Cb^{95}$	—	3.7	15.3
Mo^{99}	10.0	—	—
Ru^{103}	1.9	5.4	—
Ru^{106}	—	—	2.4
$_1Rh^{103}$	1.9	5.3	—
Rh^{106}	—	—	2.4
I^{131}	6.2	4.0	—
I^{132}	7.2	—	—
Te^{132}	7.0	—	—
Xe^{133}	12.1	3.1	—
Cs^{137}	—	—	1.5
Ba^{137}	—	—	1.5
Ba^{140}	8.8	11.1	—
La^{140}	9.3	12.8	—
Ce^{141}	4.8	11.1	—
Ce^{144}	—	1.8	26.0
Pr^{143}	8.0	11.4	—
Pr^{144}	—	1.9	26.1
Nd^{147}	4.1	4.3	—
Pm^{147}	—	—	5.7
Pm^{149}	1.7	—	—
	89.9	97.1	98.3

The turbulent behavior of the atmosphere is a more important factor in the descent of relatively small particles than gravitational settling. The descent of particles of all sizes is of course greatly hastened in the region of precipitation where, as with other atmospheric dust, transport to the earth's surface may be accelerated in several ways.

From the time the fireball begins to condense until radioactive dust actually descends to the earth, a number of processes may influence the radiochemical properties of the dust. Of course, fission products initially formed are undergoing decay and actual radiochemical composition of a sample of fallout will always depend on age of the material.

Table I lists principal isotopes present at various times following fission. When fission products are well mixed, a sample will decay in proportion to the —1.2 power of time, as noted previously. However, samples of fallout do not always decay according to this scheme. Although −1.2 is a good average figure, and as noted, is valid for well-mixed fission products, in actual practice it is observed that the slope of the exponential decay may vary between .8 and 1.8. As a matter of fact, from any given detonation, samples of fallout collected at different places are apt to decay at different rates.

This is due to the way various fission products tend to *fractionate* during the period when the fireball is formed and cooled. An important example concerns the two isotopes strontium-89 and strontium-90. Both these isotopes are derived from radioactive precursors Krypton-89 and Krypton-90 having half-lives of 180 sec. and 25 sec. respectively. Some of the radiostrontium is formed relatively late in the life of the fireball after a considerable amount of condensation has already taken place. The large particles which fall out close to a detonation are found to be depleted in radiostrontium with a corresponding enrichment in debris falling out at greater distances.

Of particular interest to water works engineers is the fractionation that may take place by water solution. Various isotopes do not dissolve uniformly but

*Presented at the Nuclear Engineering and Science Congress sponsored by Engineers Joint Council, December 12-16, 1955, at Cleveland, Ohio.

† Reprinted from the Journal, American Water Works Association, 48 No. 6 (June 1956) by permission of A.W.W.A.

there have been relatively few radiochemical studies in this field and we need more information on the way the various radioisotopes, initially present in fallout, partition themselves between suspended solids and water of a reservoir, stream or even a test tube sample.

Observations of fallout are based on the collection of airborne and settled dust samples, which can be collected with relatively simple equipment by uniform procedures.

Description of Monitoring Network

The fixed monitoring stations sample dust by collections on a 1-ft. gummed surface supported on an acetate film mounted horizontally on a frame about 3 ft. above the ground (Fig. 1). The coating retains its adhesive properties when wet, and dust particles entrapped in rain-drops are efficiently collected. Sampling is continuous and once a day gummed films are changed and mailed to the Health and Safety Laboratory in New York where their radioactivity is assayed.

The 89 cities where stations are located are listed in Table II.

The samples are prepared for analysis by ashing at 550° to 600°C. This results in a loss of some volatile isotopes, such

TABLE II

Network of Collection Stations

Location	Location
Mobile, Ala.	*Scottsbluff, Neb.
Montgomery, Ala.	Elko, Nev.
Flagstaff, Ariz.	Ely, Nev.
Phoenix, Ariz.	*Las Vegas, Nev.
*Tucson, Ariz.	Reno, Nev.
Yuma, Ariz.	Winnimucca, Nev.
Fort Smith, Ark.	*Concord, N. H.
Eureka, Calif.	*Albuquerque, N. M.
Fresno, Calif.	Roswell, N. M.
*Los Angeles, Calif.	Albany, N. Y.
Sacramento, Calif.	*Binghamton, N. Y.
San Diego, Calif.	*Buffalo, N. Y.
*San Francisco, Calif.	*New York
Colorado Springs, Colo.	(LaGuardia) N. Y.
Denver, Colo.	*Rochester, N. Y.
*Grand Junction, Colo.	Syracuse, N. Y.
Pueblo, Colo.	*Cape Hatteras, N. C.
*New Haven, Conn.	Fargo, N. D.
*Washington, D. C.	Williston, N. D.
(Silver Hill, Md.)	*Cleveland, O.
*Jacksonville, Fla.	*Medford, Ore.
*Miami, Fla.	Portland, Ore.
*Atlanta, Ga.	*Philadelphia, Pa.
*Boise, Idaho	*Pittsburgh, Pa.
Pocatello, Idaho	Providence, R. I.
*Chicago, Ill.	Charleston, S. C.
*Des Moines, Iowa	Huron, S. D.
Concordia, Kan.	*Rapid City, S. D.
Goodland, Kan.	*Knoxville, Tenn.
*Wichita, Kan.	*Memphis, Tenn.
*Louisville, Ky.	Abilene, Tex.
*New Orleans, La.	Amarillo, Tex.
Caribou, Me.	*Corpus Christi, Tex.
Baltimore, Md.	*Dallas, Tex.
*Boston, Mass.	Del Rio, Tex.
Alpena, Mich.	Port Arthur, Tex.
*Detroit, Mich.	Milford, Utah
Marquette, Mich.	*Salt Lake City, Utah
Grand Rapids, Mich.	Lynchburg, Va.
*Minneapolis, Minn.	*Seattle, Wash.
Jackson, Miss.	Spokane, Wash.
*Kansas City, Mo.	Green Bay, Wis.
*St. Louis, Mo.	Milwaukee, Wis.
*Billings, Mont.	Casper, Wyo.
Helena, Mont.	Cheyenne, Wyo.
Kalispell, Mont.	

* Stations in operation when continental tests are not in progress.

Fig. 1. Fixed monitoring station.

as those of iodine and ruthenium, but these comprise less than 10% of the total activity. This defect in procedure is justified by the simplicity of the operation.

The small amount of residual ash is transferred to plastic planchets sealed between 2 layers of vinyl tape and loaded in reels of 100 samples on automatic beta counters as shown in Fig. 2. These counters have a background of 7 to 10 counts/min. and efficiencies of the order of 10%. Samples are counted for 20 min. or for 640 counts if this occurs before 20 min. have elapsed. Blanks and standards are sealed into every tape. The counts are extrapolated to the midpoint of the sampling day and the collection is reported as disintegrations/min./ft.^{2} /24 hr.

This method of monitoring fallout is exceedingly sensitive. We have observed in field studies that a general rise in the gamma background of 10^{-4} roentgen/hr. is associated with fallout of approximately 10^6 disintegrations/min./ft.^{2}. Counting procedure permits detection of a daily fallout of as little as 10 disintegrations/min./ft.^{2}. It is thus possible to detect radioactivity producing a general elevation of background of about 10^{-9} roentgen/hr. The normal gamma background count, caused by cosmic rays, radiopotassium, radium and other natural sources of radioactivity varies somewhat in the range of 5×10^{-6} to 5×10^{-5} roentgen/hr. Thus, methods utlilized in the monitoring network enable one to estimate minute amounts of radioactivity incapable of measurably affecting general gamma radiation background of an area.

No one sampling procedure provides the ideal method for estimating deposition of radioactive dust under all conditions. The deposit on any given area will depend somewhat on the character of the surface presented. *Eg.*, when there is no rainfall, dry fallout may drift somewhat with other windblown dusts. In this situation gummed film technique may yield a high estimate of the average fallout, because it will tend to collect dust being redistributed laterally.

We have undertaken a comparison of collection effectiveness of gummed paper compared with a high walled pot. The pot was a simple stainless steel vessel 12-in. in diam. and 18-in. high. It was placed beside our gummed paper stand in New York and the contents were removed for radioassay once a week. A comparison of the radioactivity collected by the 2 methods over a period of months indicates agreement. During a 49 wk. period for which analyses of all data has been correlated, the regression of the radioactivity collected weekly by the pot, in relation to the weekly gummed paper collection was 1.17 ± 0.19. This is not significantly different from 1.

Collection methods, utilizing pots or pans for collection of total rainfall are disadvantageous in practice because of the need to transfer and handle the wet samples preparatory to shipping to a central radiochemical facility.

Findings

The cumulative findings have appeared in 2 previous reports from the Commission[1,2]. The present paper brings data up to date by including fall-

[1] M. Eisenbud and John H. Harley. Radioactive Dust From Nuclear Detonations, *Science* **117**, 141-147 (1953).

[2] M. Eisenbud and John H. Harley. Radioactive Fallout In the United States, *Science* **121**, 677-680 (1955).

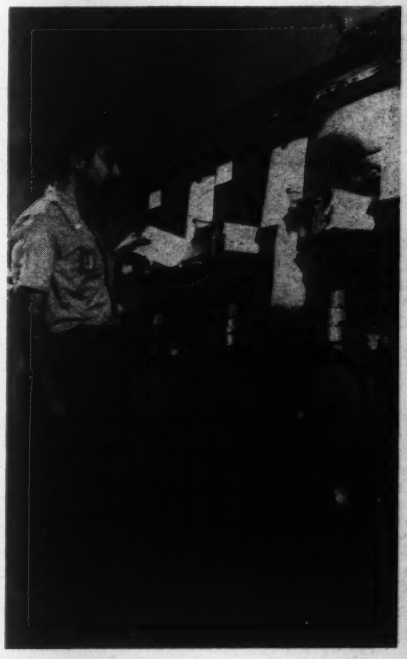

Fig. 2. Fallout samples are counted automatically by instruments that can each accommodate up to 100 samples.

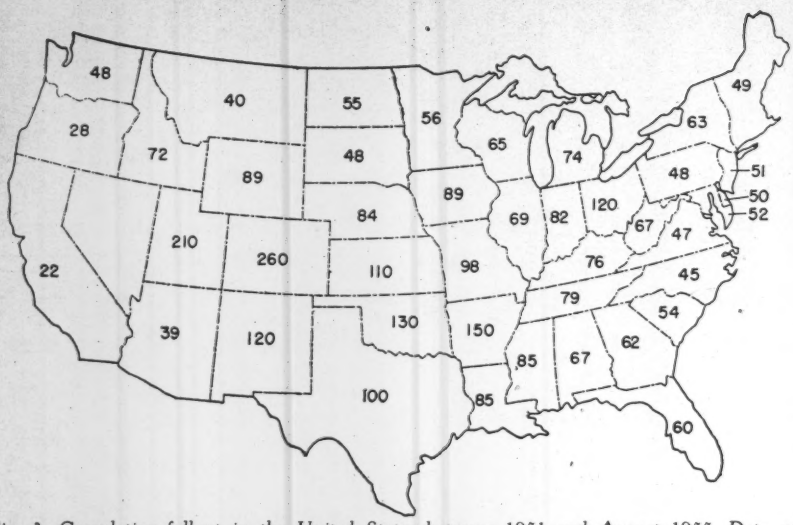

Fig. 3. Cumulative fallout in the United States between 1951 and August 1955. Data extrapolated to Jan. 1, 1956.

out observed during Operation TEAPOT, the tests conducted in Nevada during the spring of 1954.

From the start of our monitoring program until July 1955, the period covered by this report, almost 300,000 samples have been collected and assayed for radioactivity. Our cumulative data, extrapolated to Jan. 1, 1956 are given in Fig. 3 which gives our estimates of fallout for each state, except Nevada, based on data from the 89 stations listed in Table II. Nevada is not included because local fallout in the vicinity of the proving grounds is quite variable making it difficult to assign a single representative value. The total fallout varies from 22 millicuries/sq. mile in California to 260 in Colorado. These extremes are due primarily to the wind patterns that normally prevail, in relation to location of our continental test site near Las Vegas. Although the data of Fig. 3 include fallout from both the Marshall Islands and the Nevada tests, most of the fallout in the United States is from Nevada. This accounts for the low value in California, which is to the West of the Nevada Test Site and therefore not often in the path of the fallout.

The cumulative data are characterized by marked uniformity. Although there is a more than 10-fold difference between the highest values reported, the spread of values within large areas of the country is relatively narrow.

Discussion

A comparison of these data with naturally occuring radioactivity offers a useful means of appreciating meaning of the data, particularly with regard to their biological significance. Natural radioactivity originates from cosmic sources and from the naturally occurring radioisotopes, of which Ra-226, its daughter products, and K-40 are the most important.

Average concentration of Ra-226 in soil is of the order of 10^{-13} to 10^{-12} curies/gm. Taking the lower concentration as a conservative basis for comparison and limiting our consideration to the top 12 in. of the soil, one calculates that Ra-226 is present in excess of 1000 millicuries/sq. mile, greater than the total fallout reported to date.

The isotope strontium-90, which is present in fallout, is regarded as the constituent of principal biological significance, because of its relatively long half-life, 25 yr., and the fact its chemical similarity to calcium makes it possible that strontium can enter into biological systems along with calcium and ultimately be deposited in human bone. As is well known, this is also true of radium.

Analyses of samples of soil from various parts of the country discloses the strontium-90 content of the total fallout radioactivity to be in the range 1 to 5% at the present time. A representative figure for the amount of strontium-90 now present is 1 millicurie/sq. mile, or 1/1000 the amount of radium normally present in the upper foot of soil.

Although quantities of radioactivity now present are minute in relation to the radioactivity normally present in the earth's crust, the fallout is readily measureable with the radiochemical equipment available to many laboratories. The opportunity exists for valuable tracer scale experiments to study the fate of fission products in soils, reservoirs or streams. This opportunity is recognized in many universities where trace quantities of fallout are utilized to develop decontamination procedures. At other laboratories, both in universities and at AEC installations, the fate of fallout is being studied in relation to complex physical and biological interrelationships on land, in lakes, oceans, and streams.

Airborne Radioactivity Surveying: USA*†

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The ultimate objective of airborne radioactivity surveying in the U. S. atomic energy program is to locate rapidly and accurately radioactive raw materials. As such, the technique is applied primarily in a qualitative fashion; *i.e.* by detecting a sharp local increase in radiation intensity, a radioactive anomaly. Secondarily, the technique is applied in a semi-quantitative fashion by measuring small differences in radiation intensity. Such differences can then be either interpreted in terms of the grade and area of an anomalous location, or shown on isoradioactivity contour maps or profiles which suggest, by the pattern of distribution, new areas or locations warranting further examination.

Historical Review

The first document of public record pointing out feasibility of airborne prospecting is a memorandum by Bruno Pontecorvo dated Nov. 4, 1944. Airborne prospecting was first discussed in detail at a joint meeting in Washington in January 1946, attended by delegates from the U. S., United Kingdom, and the Canadian Atomic Energy groups. At that time, no experimental work had been done, and the discussion dealt largely with theoretical considerations and with the types of instrument and aircraft that might be used. Although the signal at 500 ft. air distance from a small pitchblende deposit was expected to be only 1/10,000 of the signal found by a prospector at a distance of 5 ft., because of the inverse square law, it was thought an aircraft would readily detect outcrops of sufficiently large area. By October 1948, as reported at the next joint meeting, experimental work on radioactivity measurements from aircraft had been done by all the major groups, and results looked sufficiently promising to warrant continued effort in development of instruments and methods for airborne uranium prospecting.

Early in 1949, in cooperation with Oak Ridge National Laboratory, Geiger counter equipment was installed in the U. S. Geological Survey multi-engine plane. Shortly thereafter, experimental measurements, after made at various distances above point sources of gamma radiation, indicated radiation intensity did not decrease in strict accordance with the inverse square law; the decrease followed the inverse first power of distance, a highly significant difference in behavior. Meaningful measurements could then be made at greater distances from the ground than had at first been predicted.

In August 1949, experimental radioactivity measurements were made at various flight levels over known, weakly radioactive lignites in the Red Desert region of Wyoming; these measurements, reported at the next joint meeting in September 1949, showed materials of small outcrop area containing 0.01% uranium could easily be detected at 500 ft. above the ground and at an air speed of 150 miles/hr. In June 1950, the first systematic airborne radioactivity survey of a large area was undertaken; results of this survey of 1600 sq. miles in northern Michigan were published[1] in July 1950 as a map showing the location of anomalous radioactivity together with a brief explanatory text.

Since 1951, numerous airborne radioactivity surveys throughout the states have been made by the U. S. Geological Survey, the U. S. Atomic Energy Commission, and various private companies. To date, government agencies have completed considerably more than 500,000 flight miles of radioactivity surveys and have released more than 200 maps showing the location of radioactivity anomalies in individual areas[2, 3]. No firm estimates of the number of private aircraft and the actual extent of surveying by private companies are available, largely because of the intermittent or seasonal use of light aircraft for the dual purpose of transportation and surveying. Based on reported sales of radiation detection instruments designed for aircraft or automotive installation, and on availability of contractual surveying by various companies, the number of aircraft equipped for radioactivity surveying is between 50 and 100. Presumably aircraft equipped for radioactivity surveying would be used on the average for about 100 hr. each yr. On this assumption, several hundred thousand flight miles of radioactivity surveys must be flown each yr. by private industry.

Instrumentation

Radiation detection instruments used in airborne surveying must be sufficiently sensitive to measure unambiguously a small change in radioactivity at an air distance governed by aircraft safety. A large variety of instruments is commercially available; it is no longer difficult to select a satisfactory instrument for a particular application.

As the radiation detector proper, most instruments use large-volume thallium-activated sodium iodide crystals[4] or plastic scintillators[5]. High efficiency Geiger-Muller counter tubes having a multiple-plate cathode structure are occasionally used as the detector[6]. The basic electronic circuit used with the detectors is invariably a counting rate meter, usually with variable time constant, high voltage, and discriminator settings[7]. Most amplifiers are of the

* Presented under the auspices of the American Geological Institute at the Nuclear Engineering and Science Congress sponsored by Engineers Joint Council, December 12-16, 1955, at Cleveland, O.

† Publication authorized by Director, U. S. Geological Survey.

[1] F. W. Stead, F. J. Davis, R. A. Nelson and P. W. Reinhardt. Airborne Radioactivity Survey of Parts of Marquette, Dickinson and Baraga Counties. U. S. Geol. Survey Geophys. Inv. Map. (1950).

[2] See: Geology and Mineralogy, Airborne anomaly location maps, *Nuclear Sci. Abstracts*, issued twice a month by the U. S. Atomic Energy Comm. and available from the Govt. Printing Office, Wash., D. C. Also monthly releases of Airborne anomaly location maps, by the AEC, obtainable on a subscription basis from Govt. Printing Office, Wash., D. C.

[3] See: Airborne Radioactivity Surveys. U. S. Geol. Survey Bull. 1019-E (1955); also Geology and Minerology, Airborne Radioactivity Surveys. *Nuclear Sci. Abstracts.*

[4] J. A. Harshaw, H. C. Kremers, E. C. Stewart, E. K. Warburton and J. O. Hay. Preparation and Performance of Some Scintillation Crystals. U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn. Rept. NYO-1577.

[5] F. B. Harrison, C. L. Cowan and F. Reines. Large-Volume Liquid Scintillators: Their Applications. *Nucleonics* 12, 44-7 (Mar. 1954).

[6] J. A. Tavelli. Review of Airborne Radioactivity Survey Techniques in the Colorado Plateau, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn. Rept. RMO-697.

[7] P. W. Reinhardt, C. Harris, F. J. Davis and J. Harter. Scintillation Detector for Carbone and Airborne Uses. *Nucleonics* 12, 46-7 (Dec. 1954).

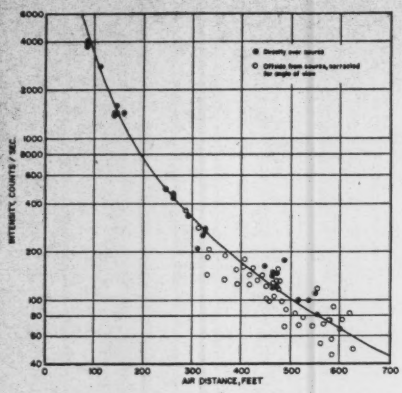

Fig. 1. Intensity from a natural point (elementary) source at various air distances from source.

continuously recording type; a few amplifiers are of the simple, direct indicating type. In addition to radiation detection instruments, equipment in multi-engine aircraft usually includes instruments for accurately locating position of the aircraft in respect to ground[8, 9].

Techniques

Airborne techniques are analogous to surface techniques in that several broad categories can be distinguished, *viz.* local, detailed, and regional surveys. Dependent upon the objectives of the particular survey and on the location of the area in respect to the operating base, helicopters, light single-engine aircraft, and long-range multi-engine aircraft have been successfully used. In selecting an aircraft, the prime requirement is that the aircraft has sufficient range to spend a significant proportion of the total flying time over the area to be surveyed.

Absorption and scattering of gamma radiation at considerable air distances from the source place an effective upper limit on the flight level of airborne surveys. The radiation intensity from a natural *point* source of radiation is decreased to less than 1/1000 at an air distance of 500 ft. Few airborne surveys are made at air distances of greater than 500 ft., and most surveys are made at air distances less than 200 ft.

The nominal flight level above ground, airspeed, and spacing of the flight path of an aircraft are intricately related and are determined largely by the particular objective of an airborne survey. The relationship among these factors is such that no optimum combination has yet been established. Our knowledge of the effect of various combinations of these factors is based largely on extensive experimental measurements, particularly those at the Grand Junction (Colo.) airport over a simulated ore occurrence, roughly 50 tons of carnotite ore at 0.35% uranium oxide in a slab 40 ft.^{2} and 6 in. thick.

As shown in Fig. 1, the intensity of gamma radiation from the ore slab decreases rapidly with increasing air distance from the source. Obviously the lower the flight level, the better is the chance of detecting a small source. However, if the airspeed remains constant, the lower the flight level the smaller is the time interval for detection of the source. To overcome this difficulty, either airspeed or time response of the detection instrument, or the combined effect of these factors must be reduced proportionately to the decrease in flight level. Thus, assuming adequate radiation detection instruments, the lower and slower the aircraft is flown, the smaller is the anomalous occurrence that can be detected.

As shown in Fig. 2, the radiation intensity from the ore slab decreases with increasing horizontal distance to the side of the source. This reflects the finite size of natural sources and the resultant decrease in solid angle of measurement as the detector moves away from directly over the source. Thus, flying at lower flight levels does not lead to a gain in detecting smaller sources far to the side of the flight path. As a generalization, width of the zone from which anomalous radioactivity can be detected is approximately twice the height of the aircraft above the ground. The lower the flight level, the smaller is the area or zone actually surveyed by an aircraft along a single flight path.

Spacing of flight lines in a given survey determines primarily the effective coverage of the area being actually surveyed for anomalies of given grade-area. For overall economy, rapidity, and broad coverage, airborne surveys should be made at the highest flight level, highest airspeed, and widest spacing of flight lines which meet the requirements established by exploration policy. In a given area and for a particular radiation detection instrument, simple empirical tests over occurrences known to be of practical significance will quickly determine maximum flight level at which the majority of similar occurrences can be detected.

Local Surveys

Local airborne surveys are essentially an extension of prospecting on foot and are qualitative in application[10]. Light single-engine aircraft are customarily used at low flight levels, usually less than 200 ft. above ground. A lightweight scintillation counting-rate meter of the non-recording type is usually adequate. Although random surveying may be done, the usual method is to follow favorable outcrops whether on a cliff face (the well-known rim flying) or on a relatively flat surface. Frequently a single flight line is flown along the outcrop, and no attempt is made to obtain complete coverage of an area. An observer, usually a geologist familiar with the area, records on a suitable base map the localities where a sharp increase in radioactivity is shown on the meter. The most successful application of low level surveying has been in and immediately adjacent to uranium mining districts such as the Colorado Plateau and the Black Hills.

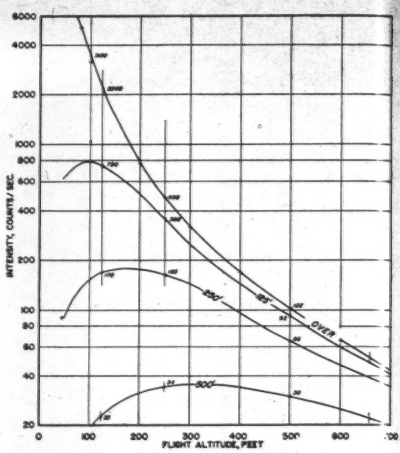

Fig. 2. Intensity from a natural point (elementary) source at various flight altitudes directly over and at 125,250 and 500 ft. off-side of the source.

Detailed Surveys

Detailed airborne surveys are best applied to areas ranging from a few sq. miles to a few hundred sq. miles that might contain extensions of known uranium deposits, or that contain rock types and structures known to be favorable. Any type of aircraft can be used at a flight level and line spacing planned to give complete coverage. The prime requirement is that the radioactivity measurements must be accurately located in respect to the ground, either by visual recognition, by photographic methods, or by radar methods. The radiation detection instruments are almost invariably of the continuously recording

[8] F. W. Stead. Airborne Radioactivity Surveying Speeds Uranium Prospecting. *Eng. Mining J.* **151**, 74-7.

[9] G. Cowper. Aerial Prospecting with Scintillation Counters. *Nucleonics* **12**, 29-32 (Mar. 1954).

[10] R. S. Foote. Airborne Exploration for Uranium. *Mines Mag.* **44**, 31-2 (Oct. 1954).

type, and the radioactivity measurements have been reported as spot anomalies, radioactivity profiles, or isoradioactivity contour maps. Although results of most detailed surveys have been released as maps showing radioactivity anomalies, results of a few surveys have been released as maps showing relatively large areas of anomalous radioactivity[11]. Isoradioactivity contour maps have been compiled from detailed surveys made by helicopter[12] and by multi-engine aircraft[13].

Regional Surveys

Regional airborne surveys covering hundreds to thousands of sq. miles differ from the detailed surveys partly in scale of operation, partly in that only partial coverage or sampling of the area is planned, and partly because the objective is to find large and new areas in which radioactive raw materials might occur. Multi-engine aircraft, equipped for determining continuously the aircraft position in respect to ground, are customarily used at a nominal 500-ft. altitude and at a flight-line spacing of at least ½ mile[8, 9]. Highly sensitive scintillation counting equipment of the continuously-recording type is used, frequently in conjunction with aeromagnetic detection equipment. The results of such surveys have been released as maps showing either spot locations of radioactivity anomalies or areas of anomalous radioactivity; occasionally data are compiled as isoradioactivity contour maps. Regional surveys have proved successful in locating new areas not known to contain uranium.

Interpretation

As currently applied, airborne radioactivity surveying is essentially a qualitative technique, that is, anomalously high radioactivity relative to the immediate surroundings is used to guide ground investigations to localities where radioactive raw materials of economic importance might occur. Further development of the technique demands that interpretation of data must be placed on a quantitative basis. To establish a satisfactory interpretation, various observable quantities measured by radiation detection instruments of the counting-rate meter type, such as the peak intensity (counts/sec.), area under the curve (total number of counts), and shape of the curve must be correlated with principal characteristics of a natural source, *viz.*, the source grade in terms of the equivalent uranium oxide content and the source configuration in terms of the surface dimensions.

The possibility of quantitative interpretation of airborne survey data is being extensively investigated[9, 14, 15, 16, 17]. As the fundamental properties of gamma radiation are well known for the energy range from natural sources, at first glance the ideal method of interpretation would seem to be based on the theoretical computation of the radiation intensities from sources of various configurations. The obvious advantage of the computation approach is that results do not have to be resolved in terms of response characteristics of the particular radiation detector. Where the radiation source is distributed in one medium, rocks, and is measured at considerable distances from the source in another medium, air, the intensity of scattered radiation predominates over that of primary radiation. This condition requires a numerical solution of the Boltzmann equation for gamma-ray transport in 2 media. Unfortunately, no satisfactory general solutions to 2 media problems in gamma-ray transport have yet been established, although the Geological Survey in cooperation with the Computing Facility of the Atomic Energy Commission at New York University is now engaged in solving the 2 media problem with plane symmetry[18].

For the present, the more feasible method of interpretation is based on a semi-empirical approach, which is admittedly restricted to data obtained with essentially identical radiation detection instruments. Based on experimental measurements at various air distances over known broad sources and over a simulated outcrop of uranium ore, an experimental or assumed form of the radiation intensity law for an elementary *point* source of essentially infinite thickness has been established. This basic expression has then been integrated over suitable geometric configurations to obtain intensities from various sources. For convenience, natural sources of infinite thickness for gamma radiation have been grouped as 2 fundamental types, the elementary *point* source (ore slab) and the infinite broad source. Three intermediate source types have been investigated:

(1) the line source which is infinitely long and of breadth less than the elementary *point* source,

(2) the slab source which is infinitely long and intermediate in breadth between the line source and the infinite broad source, and

(3) the finite source, a circular source of diameter greater than the elementary *point* source and less than an infinite broad source.

Numerical integration of expressions for source types of greatest practical interest, the slab and the finite sources, has been completed; tabulated data have been used successfully for quantitative interpretation of measurements[18]. For a scintillation-type detector of broad spectral energy response at 500 ft. above ground, the following generalizations can be made:

(1) finite sources of diam. greater than 1700 ft. and slab sources greater than 1200 ft. in breadth are infinite sources;

(2) finite sources less than 550 ft. in diam. are *point* sources;

(3) slab sources less than 800 ft. in breadth are line sources;

(4) line and slab sources must be 1700 ft. in length to be considered infinitely long. Although some error will be introduced, these conclusions can be proportionately adjusted for various flight levels; at the 100-ft. flight level a finite source of somewhat less than 110 ft. in diam. would be a *point* source.

Quantitative interpretation of data, applying the expressions developed by Sakakura[17], has proved reasonably successful. The values required for interpretation of an anomaly are the peak intensity (counts/min.) and the area under the curve (total counts). The shape of an anomaly, such as the slope and the breadth at half peak intensity, has not proved useful in interpretation.

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[8] See footnote 8, page 148

[9] See footnote 9, page 148

[11] R. M. Moxham. Airborne Radioactivity Surveys for Phosphate in Florida. U. S. Geol. Survey Circ. 230 (1954).

[12] Abraham Rosenzweig. Evaluation of the Texas Company Airborne Radioactivity Surveying at Blanding, Utah. U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn. (1952).

[13] R. M. Moxham, G. W. Walker and L. H. Baumgardner. An Investigation of Airborne Radioactivity Anomalies in the Rock Corral Area, San Bernardino County, Calif. U. S. Geol. Survey Bull. 1021-C.

[14] D. N. Peirson and E. Franklin. Aerial Prospecting for Radioactive Materials. *Brit. J. App. Physics* **2**, 281-91.

[15] J. W. Cook. An Analysis of Airborne Surveying for Surface Radioactivity. *Geophysics* **17**, 687-706.

[16] Ola Pederson. Mathematical Evaluation of Airborne Radiological Survey Data. U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn., Rept. NYO-4577 (1954).

[17] A. Y. Sakakura. Air Scattering of Gamma Rays from Thick Uranium Sources. Contrib. to Intern. Conf. on Peaceful Uses of Atomic Energy. Serial No. R. 1.1.-1039 (1955).

[18] A. Y. Sakakura. Absorption and Scattering of Gamma Radiation in U. S. Geol. Survey Trace Elements Inv. Rept. 490, Tech. Inf. Service, Oak Ridge, Tenn., pp. 296-7 (1955).

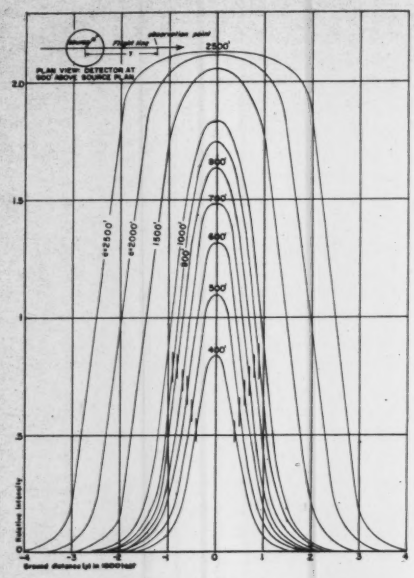

Fig. 3. Relative intensities at various distances from center of finite sources of various radii.

As shown in Fig. 3, peak intensity increases rapidly with increase in grade-area of the source, whereas the slope changes very slightly with increase in the grade-area of the source. In Fig. 4, the effect of approaching a slab source at various angles is plotted. In this case, the breadth of the anomaly changes with the angle of approach, whereas the peak intensity remains constant.

The radiation intensity from sources measured on two or more adjacent flight lines can be satisfactorily interpreted to within a few thousandths of a % equivalent uranium. Such interpretation has been amply confirmed by field investigations; *eg.* airborne radioactivity measurements made at 500 ft. above a shale were interpreted at 0.0017% equivalent uranium, and laboratory analyses of representative shale samples showed 0.001-0.002% equivalent uranium[19].

Where measured on a single flight line and not observed on adjacent flight lines, the radiation intensity from a natural *point* source or from a finite source has proved difficult to interpret in terms of the grade and the area. The combined grade-area can be determined, but no simple means of distinguishing between a small high grade ore and a large area of slightly abnormal radioactivity has as yet been developed. However, for a given flight level and flight line spacing, it is possible to determine the limits of detection. Extrapolation from the experimental data shows that at a nominal 500-ft. flight level and at a line spacing of 1/4-mile, the minimum detectable source located midway between flight lines would be an ore-grade body (at 0.1% uranium oxide) with a minimum radius of 60 ft.

The possibility of discriminating by spectral energy measurements whether a particular source is preponderantly uranium, thorium, or potassium, or various mixtures thereof, has been investigated. The Oak Ridge National Laboratory has recently completed spectral energy measurements of :

(1) uranium in equilibrium, in a selected pitchblende sample,

(2) uranium in equilibrium, in a thick source consisting of large blocks of Chattanooga shale, and

(3) thorium in equilibrium, in thorium nitrate samples prepared in 1906 and 1922. These measurements indicate that gamma-ray spectrum from thick natural sources is much degraded by internal scattering and absorption of radiation. As in a degraded spectrum many of the peaks are completely obliterated and others are much diminished, spectral energy discrimination of the radioisotopes in thick natural sources is at best difficult and is not presently attractive from a practical viewpoint. For natural sources of significantly high thorium content, it might be possible to determine the presence of thorium in a qualitative fashion.

Summary

Airborne radioactivity surveying has proved to be a rapid and effective means of prospecting for radioactive raw materials. It has been applied successfully both on a qualitative and a semi-quantitative basis.

Considerable progress has been made in establishing quantitative interpretation of airborne radioactivity measurements in terms of equivalent uranium content and areal extent of natural sources. Further development and wider application of the technique will undoubtedly occur as the quantitative interpretation of measurements becomes firmly established.

At present, airborne radioactivity surveying is restricted to detecting and measuring abnormally high concentrations of radioactive raw materials exposed directly at the surface. Recent data suggest that in metamorphic and igneous terranes uranium deposits occur in large but localized areas where the radioactivity of the country rock is slightly but significantly different from adjacent areas of similar rock types. The target or favorable areas in crystalline rocks might be measurable in sq. miles rather than in terms of a local concentration of a few hundreds of sq. yd. as in the case of sedimentary terranes. The possibility of locating such large targets is highly attractive, particularly as interpretation of broad semi-infinite source data is much simpler and more accurate than is interpretation of *point* and finite source data. Where the objective is to determine the distribution pattern of radioactivity over large areas, regional airborne surveys can be made at wide spacing of flight lines and at high flight level, possibly at the 1000-ft. level.

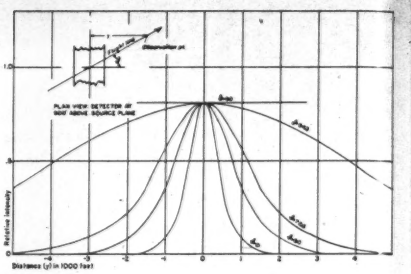

Fig. 4. Relative intensities at various distances (y) from center lines of a slab source 400 ft. wide at various angles of approach.

Acknowledgments

This paper was prepared as part of a program being conducted by the U. S. Geological Survey on behalf of the Divisions of Raw Materials and Research of the U. S. Atomic Energy Commission. Much of the development has been a joint undertaking of the Oak Ridge National Laboratory, the A. E. C. Computing Facility at New York University, and the Geological Survey.

[19] A. Y. Sakakura. Absorption and Scattering of Gamma Radiation in U. S. Geol. Survey Trace Elements Inv. Rept. 440, Tech. Inv. Service, Oak Ridge, Tenn., pp. 242-3 (1954).

Meteorology as Related to Reactor-Site Selection*†

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Development of atomic energy into a major technological activity presents an important challenge to meteorologists' ingenuity, especially in connection with site selection and operation of reactor facilities. Radioactivity, when confined and properly shielded, is of direct concern only to persons in the immediate area. It is not until it escapes or is released into the air that location of the site with respect to its surroundings becomes extremely important. Since the atmosphere is the most mobile of all geophysical media and can transport radioactivity swiftly over large areas, meteorology assumes particular importance in site selection and hazard analysis of proposed atomic energy installations[1]. Since it is evident to the meteorologist certain locations[2], because of their geographical or physical location, may expect to receive large concentrations of pollutants, it is a recommended practice to evaluate air pollution potential, or dilution efficiency of the atmosphere at prospective locations before making a final decision on just where the plant will be located.

In assessing requirements for an atomic energy site, one must understand the final plant design. Chemically toxic radioactive waste gases may be produced by a nuclear reactor through irradiation of cooling air or periodic removal of fission product gases and their release to the air. Laboratories handling radioactive materials may also find it necessary to vent their hoods and working spaces. Large chemical plants preparing or reprocessing nuclear fuels may be forced to dispose of large quantities of fission gases; they may also be required to use and release toxic chemicals in gaseous form. The evaporation of radioactive liquid wastes may cause a waste *burial ground* to be a source of gaseous contaminants. Incineration of radioactive solids can contribute to gaseous products. The method of release of these gases is almost as numerous as the sources. They may be deliberately exhausted through stacks or vents, they may inadvertently leak from containers or buildings, or they may be evaporated from water surfaces. For most of the reactor power plants now in the process of being developed, only limited quantities of radioactive off-gases will be routinely released, so any proposed site must be evaluated mainly for a possible accidental rupture of the containment vessel. However, other atomic energy installations may be operated by industry within the next few years, requiring daily disposal of radioactive waste gases. Sites for this type of facility must be examined from a consideration of the immediate environment.

Meteorology is not usually a primary factor in selection of a new site. Many factors such as market, raw material, water and power availability, labor and construction costs must be considered, all of which may be more important than weather effect. However, the problem of waste disposal, either as it affects the streams or the atmosphere, must be evaluated[3]. In the case of radioactive wastes from a nuclear plant, meteorology is usually given slightly more consideration.

Meteorological Parameters

Those meteorological parameters which should be considered at those locations where atmospheric effluents will or may be released, are wind direction and speed, atmospheric stability as given by the vertical temperature distribution (called lapse rate) and precipitation records. The data on wind and stability are usually analyzed to give a picture of average conditions and the variation with time of day and season. One such type of presentation is shown in Fig. 1. Fig. 2 presents an annual distribution of lapse rate vs. time of day. Such a graph is obtained by averaging the lapse rate for each hour for the 4 seasons and the constructing isopleths of equal lapse rates. Another useful statistic is the duration of temperature inversions (increase of temperature with height). These particular data are probably most useful in comparing two alternate sites from the standpoint of utilizing the atmosphere for disposal of gases. A site where the bias is toward longer duration of temperature inversions when wind direction is toward populated areas would be less adapted to gaseous waste disposal than one where inversions were less frequent and persistent. Meteorological factors considered alone will seldom permit a categorical determination of suitability of a site. The type of plant operation must certainly be considered. In the case of persistent inversions mentioned above, if a particular plant has sufficient storage capabilities, and if toxic levels are low enough, a large proportion of inversion conditions may not be a serious drawback to location of the plant at this site. Certainly however, the increased concentrations that might result under unfavorable meteorological conditions must be examined before such a decision is reached.

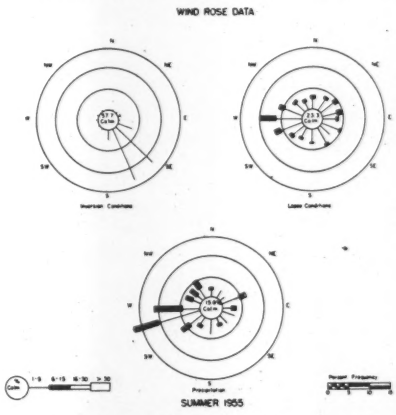

Fig. 1. Wind distributions at one station under inversion and lapse atmospheric conditions and during precipitation periods.

Meteorological Diffusion

Evaluation of the numerous influences affecting dispersion of gases in the atmosphere requires some type of coherent mathematical statement containing parameters responding to physical changes of the atmosphere near the source and, in addition, that can be applied to sources in widely differing locations. There are several mathematical treatments of diffusion in the atmosphere, no one of which seems to satisfy all the variables that may influence diffusion. However, the development and formulation due to O. G. Sutton of England[4] have been applied to dispersal of stack gases at many of the Atomic Energy Commission sites in the U. S. Sutton's instantaneous point source formula is:

[1] U. S. Atomic Energy Commission. Meteorology and Atomic Energy—A Manual (1955).

[2] U. S. Public Health Service. Air Pollution in Donora, Pa., Bull. No. 306. Govt. Printing Office (1949).

*Presented at the Nuclear Engineering and Science Congress sponsored by Engineers Joint Council, December 12-16, 1955 at Cleveland, Ohio.

† Published J. Sanitary Engineering Div., *Proc.* American Society Civil Engineers Paper 1001 (June 1956).

[3] S. M. Stoller. Site Selection and Plant Layout. *Nucleonics* **13**, 42-5 (June 1955).

[4] O. G. Sutton. The Theoretical Distribution of Airborne Pollution from Factory Chimneys. *Quart. J. of the Roy. Meteorol. Soc.* 73, 426 (1947).

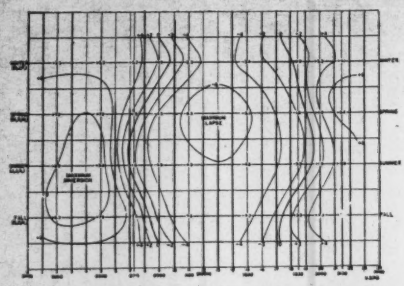

Fig. 2. Seasonal variations in the average thermal gradient between 5 and 400-ft. levels. Temperature sounding data for the year Sept. 1950 thru Aug. 1951. Central Facilities (WBO).

$$\chi_{(x\,y\,z\,t)} = \frac{Q}{\pi^{3/2} C_x C_y C_z (ut)^{3(2-n)/2}} \exp \left\{ -(ut)^{n-2} \left(\frac{x^2}{C_x^2} + \frac{y^2}{C_y^2} + \frac{z^2}{C_z^2} \right) \right\} \quad (1)$$

where x, y, and z (m.), are co-ordinate axes in the downwind, cross wind, and vertical directions, Q is the source strength (curies, gm., etc.) u is the mean wind (m./sec.), t is time (sec.), C_x, C_y, C_z are *virtual diffusion coefficients* $[(m.)^{n/2}]$, and n is a dimensionless stability parameter variable between zero and one with increasing values corresponding to increasingly stable atmospheric temperature gradients.

By integration with respect to time, a formula for a continuous point source is obtained.

$$\chi_{(x\,y\,z)} = \frac{2Q}{\pi\, C_y\, C_z\, u\, x^{2-n}} \exp \left\{ -x^{n-2} \left(\frac{y^2}{C_y^2} + \frac{z^2}{C_z^2} \right) \right\} \quad (2)$$

By integration with respect to direction, usually cross wind (y-axis), an equation describing the concentration distribution downwind from a continuous line source results.

$$\chi_{(x\,z)} \quad \frac{2Q}{\pi^{1/2} C_z\, u\, x^{(2-n)/2}} \exp \left\{ -\frac{h^2}{C_z^2\, x^{2-n}} \right\} \quad (3)$$

where h = height of release (meters)

Fig. 3a shows concentration isopleths calculated from equation (2), and 3b from equation (1).

Certain useful geometrical properties of diffusing clouds are easily obtained by differentiating and maximizing certain of Sutton's results.

The distance of the maximum concentration from the source (represented by d_{max}) for an instantaneous point source is

$$d_{max} = \left(\frac{2h^2}{3C^2} \right)^{1/(2-n)} \quad (4)$$

and for a continuous point source is

$$d_{max} = \left(\frac{h^2}{C^2} \right)^{1/(2-n)} \quad (5)$$

while (for the instantaneous point source) the maximum concentration at the point d_{max} is

$$\chi_{max} = \frac{2Q}{(2/3e\pi)^{3/2} h^3} \quad (6)$$

and for the continuous point source is

$$\chi_{max} = \frac{2Q}{e\pi\, uh^2} \quad (7)$$

The cloud width, $2Y_0$, and the cloud height Z_0 are easily obtained from

$$2Y_o = 2 \left(\ln \frac{100}{p} \right)^{1/2} C_y\, (x)^{(2-n)/2} \quad (8)$$

$$Z_o = \left(\ln \frac{100}{p} \right)^{1/2} C_y\, (x)^{(2-n)/2} \quad (9)$$

where p is any desired percentage of the axial concentration. These formulae represent one set of primary tools of a meteorologist in attempting to describe the travel and dispersion of gaseous wastes.

However, these formulae together with paratmeters obtained by Sutton were developed under conditions which may differ greatly from those where computations must be made. It must be remembered that parameters were based on 3-min. average concentrations. Secondly, terrain over which the experiment was conducted was relatively smooth. And third, the equations were developed for neutral temperature gradient conditions. If these factors are always considered, the equations may be used with a fair degree of success, and meteorological uncertainties are seldom greater than other factors such as rate and amount of released effluent.

Holland[5] has shown that diffusion coefficients may be modified experimentally to correspond to the site over which gaseous effluent is released. A more empirical approach was adopted by Church[6] in which behavior of effluent plumes from more or less isolated stacks was classified according to appearance and the type of vertical temperature gradient usually accompanying various plume types. These types and the accompanying temperature lapse rates[7] are shown in Fig. 4. In general this approach requires qualitative adjustment to the diffusion formulae; however, it is possible to correlate plume-type behavior with parameters of the equations and obtain concentration estimates correct to an order of magnitude.

Particular mention should be made of behavior of waste gases from an elevated source under stable atmospheric conditions, since in these instances diffusion formulae are subject to greatest error. Field experiments with visible smoke plumes show when the atmosphere is stable, effluent from an elevated source will travel long distances with negligible vertical diffusion and only slow horizontal spreading. In fact, the horizontal spread is more the result of meandering variation in wind direction than of eddy dispersion of the plume. The plume, when viewed from above or below, resembles a long thin ribbon which widens slowly with distance. Significance of this type of dispersion pattern is readily seen, since material released is diluted slowly and concentrations aloft may remain high for several kilometers. Should this highly concentrated plume intersect higher terrain or be brought suddenly downward by precipitation, appreciable ground concentrations will be much greater than predicted theoretical values.

(a) *Surface concentrations for continuous release from 50 m.*

(b) *Successive surface concentrations for instantaneous release from 50 m. (8 min., 23 min., and 53 min.)*

Fig. 3. Isopleths of ground concentration (from Sutton formulae).

In addition to choosing favorable meteorological conditions for release of gaseous waste products, it can be seen from the formulae of (6) and (7) that the maximum ground concentration is inversely proportional to the height of the point of release. It is therefore desirable to vent the material through stacks as high as possible. However, there is a practical and economical limit to the height of a stack. In an attempt to extend the height of release without building prohibitively high stacks, use is often made of blowers to increase exit velocity of the gas or heaters to increase its temperature, thus its buoyancy, and obtain additional height before lateral diffusion takes over. Before expensive equipment for heating or accelerating gaseous wastes is installed, it is well to examine prevailing meteorological conditions since both excess temperature and increased velocity of exhausted gases are most effective when horizontal wind is light. At a location subject to a persistent high wind speed, the gain in *effec-*

[5] J. Z. Holland. A Meteorological Survey of the Oak Ridge Area. U. S. Atomic Energy Rept. ORO-99 (1953).

[6] P. W. Church. Dilution of Waste Stack Gases in the Atmosphere. *Ind. Eng. Chemistry* 41, 2753-6 (1949).

[7] P. A. Humphrey and E. M. Wilkins. The Climatology of Stack Gas Diffusion at the National Reactor Testing Station. U. S. Atomic Energy Rept. IDO-10020 (1952).

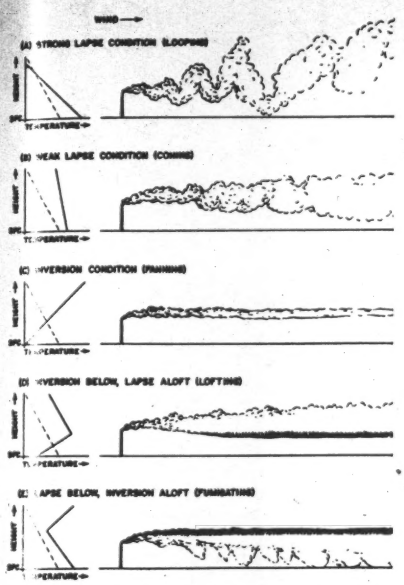

Fig. 4. Schematic representation of stack gas behavior under various conditions of vertical stability.

tive stack height from auxiliary equipment may be quite small.

Meteorological Observation, Application and Conclusions

After a definite location has been chosen, more specific information can be obtained by installation of a program of meteorological measurements at the site. This program will usually consist of records of wind, temperature, precipitation, and, if required, temperature lapse rates. The scope of such a site meteorological program will depend on several factors; *Viz,* magnitude of the potential pollution sources, size of the site, and roughness of the terrain. A large site with many nuclear installations, or one in very irregular terrain, will require a more elaborate meteorological program to define diffusion patterns than would a single laboratory located in a large level plain. The meteorological data may be of routine value in evaluating radiation measurements or for legal purposes in addition to engineering value for plant expansion.

Specific applications of meteorology to the problem of gaseous waste disposal will include 2 main fields, engineering design and plant operations. In the field of engineering design, meteorological information may be used to select a favorable site for the use of the atmosphere to dispose of waste gases. Information may be furnished on the placement and orientation of buildings at a site so that no one building is persistently affected by gases from another source. If the character of a site is such that lateral dispersion is limited, buildings may be spaced (based on the theoretical equations and actual meteorological data) to avoid points of maximum concentrations. If computations indicate untreated gases will result in concentrations higher than desirable, meteorological data can be considered in the choice of stack heights sufficient to obtain tolerable concentrations without unnecessary expenditures. In this connection, it should be noted that information of the average height of temperature inversions may be quite valuable. If the majority of inversions lie below a reasonable height, stacks may be constructed to vent gases above the inversion, thus obtaining the increased dilution of the more unstable air aloft and utilizing the inversion barrier to prevent the downward spread of contaminants. Without precise meteorological information, it would be difficult to obtain such an advantage other than by chance. In addition to the use of tall stacks, the volume and/or toxicity of waste gases may be reduced by absorbers, filters, scrubbers, *etc.* Capacity of these devices may be fitted to the capacity of the atmosphere at a particular location and time to disperse materials. In applying meteorological data to plant operation, the meteorologist may be asked to compute concentrations resulting from specific operations; and, if necessary, a program may be instituted to control operations based on meteorological information. Such control could consist of limiting effluent vol. so ground concentrations are kept below a certain value. Or the release of waste gases may be scheduled only for times when meteorological conditions favor the rapid spread and dilution of released material. An initial survey of an area and correlation of favorable diffusion conditions with specific indications of meteorological instruments may provide sufficient information. One such approach which would not necessarily require meteorological personnel has been described by Smith[8]. This work correlated the width of the wind direction trace with the temperature lapse rate. However, considerable testing at various locations is required before complete reliance can be placed on this method. Another and more direct approach has been to couple an anemometer to controls of a venting operation so when the wind direction is unfavorable, the release of gases is automatically halted. It is evident many nuclear processes are not amenable to this type control.

In addition to engineering applications, meteorology has significance to a practice largely confined to the atomic energy industry, *i.e.* the routine monitoring of airborne radioactivity. Using meteorological data, monitoring stations may be sited in the prevailing wind directions and at locations where the highest concentrations are likely to occur. If this is not practical, it is possible to combine monitoring and meteorological data and arrive at accurate concentration for locations where measurements were not obtained. Since fixed monitoring stations may not provide all desired coverage, it is practice to have mobile units able to monitor specific releases. If this practice is to be of maximum value, these mobile units should be vectored into position on the basis of current and expected meteorological conditions.

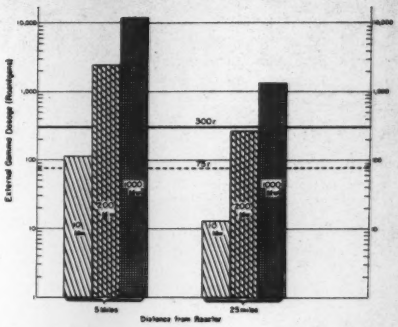

Fig. 5. Gamma radiation from fission product cloud.

It is necessary to mention the role meteorology can play should a nuclear reactor accident result in the release of fission products to the air. Higher powered reactors operating for long times contain enough fission products to seriously overload the dilution capacity of the air. The external gamma dosage alone from high power reactor debris clouds can be dangerous miles from the point of release. Fig. 5 illustrates the external gamma dosages along the centerline of cloud travel computed using Holland's technique[1]. These computations assume a) long reactor lifetime, b) 100% instantaneous release of the contained fission products c) release at ground level in stable conditions with a 4 mph. wind. Meteorology would enter into an accident of this magnitude in formulating disaster warning plans and by delineating areas and dosages covered by the cloud for various meteorological conditions. If at the time of such an accident it appears radiological hazards may exist many miles from the site, it is mandatory that immediate information on current wind direction and speed be available to plan warnings and evacuations. Also, forecasts must be made to

(Continued on page 170)

[8] M. E. Smith. The Forecasting of Micrometorological Variable. *Am. Meterol. Soc. Meteorol. Mono.* 1, 50-5 (Nov. 1955).

[1] See footnote 1, page 151.

Comparative Study of Oxidants in the Los Angeles Atmosphere*

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and
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We have made an analysis of the Los Angeles smog with respect to one of its primary manifestations, the presence of *oxidant*. Previous studies[1,2,3] have indicated that periods of smog are characterized by high oxidant values. Data for the analysis were obtained from 4 instruments which sampled Pasadena atmosphere for the period July 15—Nov. 15, 1955. This location and period of sampling were chosen because, as shown in footnote 2, Pasadena is an area of high incidence of smog this particular time of year, making it possible to get the maxima of data for the shortest possible sampling schedule. The 4 instruments used were, a phenolphthalin oxidant apparatus, a potassium iodide continuous oxidant recorder, a rubber cracking apparatus, and an ozone ultraviolet spectrometer. All of this equipment was situated on the California Institute of Technology campus within a distance of 325 ft. of each other. The phenolphthalin apparatus was operated by A. J. Haagen-Smit and M. M. Fox on the first floor of Kerckhoff Laboratories; the potassium iodide continuous oxidant recorder and the ozone rubber cracking apparatus were operated by the Field Group of the Air Pollution Control District on the roof (4th floor) of West Bridge Laboratory of Physics; and the spectrometer was operated between Kerckhoff and Bridge Laboratory roofs by Borman Engineering, Inc. under contact to the Air Pollution Foundation.

Definition of Oxidants

The term *oxidant* is rather an elastic one, meaning different things in different places. The most exact definition can be formulated as: *An oxidant in air is a substance whose oxidation potential is higher than that of the ordinary oxygen (O_2) in the same air, both taken at the concentrations actually present in the mixture being analyzed.* Since it is often inconvenient to measure the oxidation potential of constituents in air, the following definition is frequently substituted: *an oxidant in air is a substance capable of oxidizing a reference substance, said reference substance being incapable of being oxidized by ordinary atmospheric oxygen.* This second definition is of such importance that it must be understood; it is the one which will be used throughout this report.

This definition is based on a reference substance, and whether or not a substance meets the definition depends to a considerable extent on the reference substance chosen. For this reason we find somewhat different results with different substances. For convenience the reference substance is usually an aqueous solution of a reducing agent. Therefore, the properties of the reference substance depend not only on the reducing agent used, but also on the concentration of the solution, the pH of the solution, temperature, and other factors.

In the determination of oxidants, the air is brought in contact with the reference solution and the amount of the latter which is oxidized is measured. This determination of oxidants is empirical, and numerical results are comparable only when determinations are made exactly in the same way. Also they must be considered as measuring the condition of the air rather than the exact amount of any specific substance.

The closer the reduction potential of the reference solution approaches the oxidation potential of atmospheric oxygen, the closer the second definition will approach the first. Individual reference substances will be discussed in the section dealing with Laboratory response studies.

Total versus Net Oxidants

Smog contains both oxidizing and reducing agents. The oxidizing power of smog may be considered either as the total amount of oxidants without any allowance for the reducing agents present, or as the net amount of oxidizing agents present after (assumed) reaction with (potential) reducing agents. These two values are often widely different and in considering any data on oxidants it is necessary to know whether a net or total figure is being measured.

One phase in the above description of net oxidants needs further explanation, namely *after reaction with the reducing agents.* In the gas phase, reducing and oxidizing substances in the concentrations found in polluted air can co-exist for considerable time because of their low reaction rates. For example, air may contain both ozone, an oxidant, and sulfur dioxide, a reducing substance.

When air containing both oxidizing and reducing materials is passed through a reagent, the extent and nature of the reaction will depend both on substances in the air and nature of the reagent. The reaction will rarely conform stoichiometrically with any simple equation. For these reasons corrections applied to net oxidants to convert them to total oxidants are empirical.

In the reported data, the chemical methods of analysis give a net oxidant. To get a total value one must add to this net value the amount of oxidant lost by reaction with reducing substances, but this correction factor is empirical and often difficult to make. Under present conditions in the Los Angeles basin, the uncorrected net value does correlate with smog severity.[2]

One of the principal oxidants of concern in this study is ozone, the triatomic form of oxygen, a highly reactive and oxidizing material. It is considered a normal component of the earth's atmosphere of variable concentration averaging between 1-3 pphm. (by vol.). Most polluted atmospheres are devoid of ozone since they are apparently in the main reducing atmospheres. However, in Los Angeles, ozone is the only oxidant which has been well identified; other oxidants have either been postulated or suspected to exist.

Instrumentation

The phenolphthalin method for measuring oxidant has been described in a preliminary report.[4] It is based upon the oxidation of phenolphthalin ($C_{20}H_{16}O_4$)

[1] Second Technical and Administrative Rept. Air Pollution Control in Los Angeles County, 1950-51. Air Pollution Control District, Los Angeles County (1951).
[2] N. A. Renzetti., ed., An Aerometric Survey of the Los Angeles Basin August-November, 1954. Report No. 9, Air Pollution Foundation, Los Angeles (July 1955).
[3] The Smog Problem in Los Angeles County. Stanford Research Inst., Los Angeles (1954).
* Presented at the 49th Annual Meeting of APCA, Buffalo, N. Y., May 20-4, 1956.
[4] Louis C. McCabe. Atmospheric Pollution. *Ind. Eng. Chem.* **45**, 111A (September 1953).

Fig. 1. Phenolphthalin oxidant apparatus.

to phenolphthalein ($C_{20}H_{14}O_4$) by the oxidant present in the atmosphere. The concentrated phenolphthalin reagent is diluted with distilled water to which copper sulphate is added. This mixture is placed in a bubbler, and air at approximately 1 *l.*/min. is passed through for 10 min. The color developed is read on a standard colorimeter using a green filter (No. 54) on a Klett Summerson colorimeter. Oxidant concentration can be estimated from a standard curve. The standard curve is developed by using dilute solutions of 30% hydrogen peroxide for the concentration range of interest 0-100 pphm. (by vol.). Fig. 1 shows a photograph of this equipment.

The principle of the potassium iodide recorder has been described.[5] The instrument consists essentially of 2 parts; a continuous air-liquid contacting column, and a recording colorimeter. Its operation is based on the liberation of iodine from a buffered neutral (pH=7) potassium iodide solution by the oxidant in the atmosphere. The light transmission of the reacted solution is measured by a photocell colorimeter and is continuously recorded on a strip chart recorder. The reacted solution passes from the colorimeter through an activated carbon filter to effect regeneration of the iodide solution. By maintaining air and liquid flow rates constant it is possible to calibrate the instrument directly in terms of ozone. Calibration of this system is effected by putting known amounts of iodine in 20% potassium iodide directly into the colorimeter cell and developing a graph of absorbance (at 3550 Angstrom) versus concentration of iodine (0-100 micro equivalents). Then the equivalents of iodine may be related to the equivalents of ozone since the overall reaction appears to be $O_3 + 2KI + H_2O \rightarrow O_2 + I_2 + 2KOH$. As operated in this survey an air flow rate

[5] F. E. Littman and R. W. Benoliel. Continuous Oxidant Recorder. *Anal. Chem.* **25**, 1480-3 (October 1953).

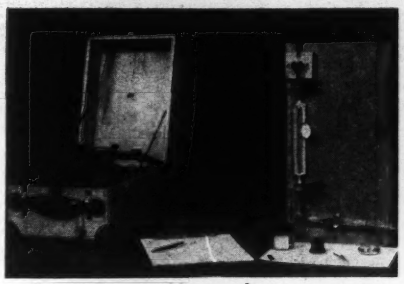

Fig. 2. Ozone rubber cracking apparatus.

of 5 *l.*/min. and liquid flow rate of 5 ml./min. were maintained.

The principle of using the cracking of rubber for ozone measurement has been discussed in footnote 6. As used in this survey atmospheric concentrations of ozone were obtained by observing the time required for initial cracking on a calibrated strip of rubber placed under tension in the air stream. A flow rate of 1 or 1½ *l.*/min. was maintained by a suitable pump and flowmeter. The rubber stock is calibrated against a known concentration of ozone produced in an ozonizer and measured by iodine released from a 2% KI solution. Fig. 2 shows a photograph of this apparatus.

The ozone ultraviolet spectrometer has been discussed briefly in footnote 7. Basically the method makes use of the strong absorption by ozone of ultraviolet radiation in the region 265-280 mμ and practically negligible absorption at 313 mμ. A beam of ultraviolet light is projected across a 325 ft. atmospheric path to a quartz spectrometer where the intensity is measured as a function of wavelength. Readings for each wavelength were obtained twice every 15 min. throughout the 24 hr. period. In order to minimize the effect of other attenuants and particulate scattering ratios of intensities $\frac{I_{Gamma1}}{I_{Gamma2}}, \frac{I_{Gamma3}}{I_{Gamma1}}$ for the 3 wavelengths $\lambda_1 = 265$ mμ, $\lambda_2 = 313$ mμ, $\lambda_3 = 280$ mμ, are used to determine ozone concentrations. Calibration is normally effected by using night-time

[6] C. E. Bradley and A. J. Haagen-Smit. The Application of Rubber in the Quantitative Determination of Ozone. *Rubber Chem. Technol.* **24** (4): n.p. (Oct.-Dec. 1951).

[7] N. A. Renzetti. Ozone in the Los Angeles Atmosphere. *J. Chem. Phys.* **24**, (4): 909 (April 1956).

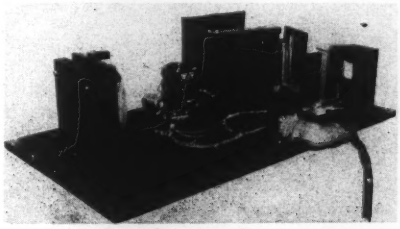

Fig. 4. Optical system of spectrometer.

Fig. 3. Ozone ultraviolet spectrometer.

(12-4 AM) ratios as essentially zero ozone concentration. Laboratory-determined absorption coefficients accurate to about 1% are used in the computation. Fig. 3 shows the equipment. On the left is the light projector; in the center is the receiver consisting of the spectrometer, detector, and electronics; on the right is the strip chart recorder. Fig. 4 shows the optics of the spectrometer itself.

Methods of Sampling the Atmosphere

The phenolphthalin oxidant apparatus as used in this survey was operated daily from July 15 to November 15 about 8 AM to 6 PM. The atmosphere is sampled each hour at 1 *l.*/min. for 10 min. Data as reported represents the concentration of oxidant in a 10 *l.* sample of the atmosphere taken hourly.

The potassium iodide oxidant recorder was operated continuously on a 24 hr. basis for the entire period of the survey. The atmosphere was sampled at 5 *l.*/min. A continuous trace of oxidant concentration vs. time was obtained on the strip chart recorder. Data presented in this study were obtained by taking hourly readings, averaging them for each hr. and plotting the resulting value for each hr. on the half hr. However, as indicated in footnote 8 there is a considerable time lag in the response on the chart to the actual concentration of oxidant in the atmosphere because of the finite liquid flow rate and liquid capacity of the colorimeter. For rapid large changes in oxidant concentration the recorder may lag 10-20 min.

The rubber cracking apparatus was used to measure the atmospheric ozone; it was operated only at times of predicted high smog conditions during middle hours of the day. Since the degree of cracking depends on both the concentration and time of exposure, sampling times varied from 1-20 min. and the corresponding sampling vol. were 1-30 *l.* Readings were taken every 15 min. to 1 hr. depending on how fast the ozone concentration was rising.

[8] W. J. Roberts and S. H. Judd. Concerning the Beckman Continuous Oxidant Recorder (COR). Memorandum to A. T. Rossano, Jr., California State Department of Public Health (June 15, 1955).

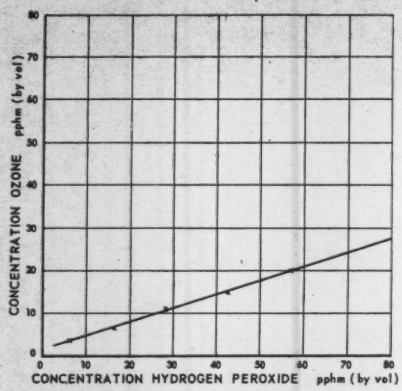

Fig. 5. Relative Response of Phenolphthalin to Ozone and Hydrogen Peroxide (Laboratory). LACAPCD Test No. D-40, Dec. 1954.

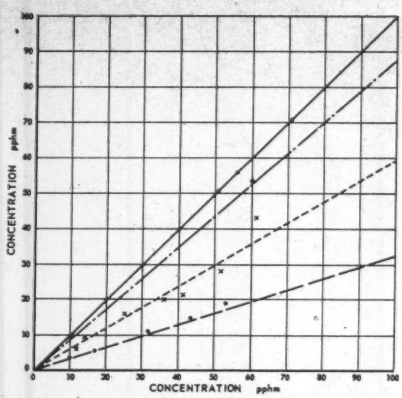

Fig. 6. Relative Ozone Response Graphs (Laboratory). Calif. Inst. of Tech. A. J. Haagen-Smit, March 1956.

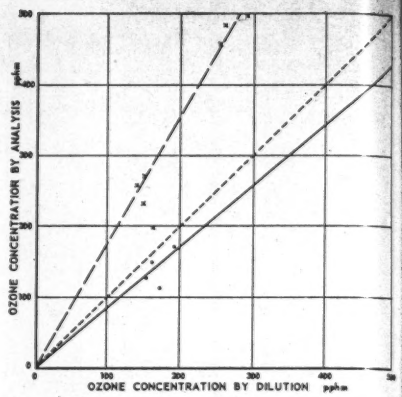

Fig. 7. Ozone Response Graphs (Laboratory). Armour Research. Feb. 20, 1956.

The ozone ultraviolet spectrometer was run continuously night and day throughout this period. As indicated above, two essentially instantaneous determinations of ozone are obtained every 15 min. Data as presented in this study were based on the average of 8 instantaneous readings for each hour.

In summary of sampling methods, one should note that whereas the chemical methods perform integrations in time (1 to 20 min.), the spectroscopic instrument performs an integration over space (*i.e.* the 325 ft. optical path). Some differences in the response curves might be attributed to these variations.

Laboratory Studies and Calibrations

In view of the fact that previous evidence indicated that the primary component of the oxidant in the Los Angeles smog is ozone, it seemed reasonable to relate relative responses of various chemical systems to gaseous ozone in air. When one does this, one runs into rather difficult chemistry and somewhat surprising results.

In using phenolphthalin reagent for the measurement of oxidant in the range of concentration of 0-100 pphm. (by vol.), normal practice has been to develop the calibration curve of color (optical density) with known concentrations of hydrogen peroxide. One then reads optical density of the phenolphthalin which has reacted with air to obtain the concentration of oxidant therein.

Experiments using this method of calibration and measuring the response of the phenolphthalin reagent to an ozone-in-air stream have been carried out in three separate laboratories.

B. Levy[9] obtained results shown in Fig. 5. This data yields a ratio of phenolphthalin response to ozone to that of hydrogen peroxide of 2.25. The ozone-in-air stream was monitored with iodine release in a 2% potassium iodide bubbler apparatus. The iodine released was measured by the titration method. Phenolphthalin reagent would indicate 2.25 times the actual amount of ozone if one used the peroxide calibration. We have indicated this result in the first line of Table I.

TABLE I
Laboratory Data

Reagents	Ratio of Response
Phenolphthalin (1 bubbler) Potassium iodide 2%+	2.25[a]
Phenolphthalin (1 bubbler) Potassium iodide 2%*	2.62[b]
Phenolphthalin (3 bubbler) Potassium iodide 4% (buffered)*	2.10[c]
Phenolphthalin (3 bubbler) O_3 (dilution)	1.75[c]
Potassium iodide continuous oxidant recorder (Beckman)* Potassium iodide 2%+	1.13[a]

(a) Los Angeles County Air Pollution Control District
(b) A. J. Haagen-Smit
(c) Armour Research Foundation
Note: + Iodine release by titration.
Note: * Iodine release measured colorimetrically.

Haagen-Smith carried out similar experiments not only with phenolphthalin but also with 2% and 20% potassium iodide in distilled water and 20% potassium iodide buffered. The samplers were all bubblers and the amount of iodine released was determined colorimetrically. His results are summarized in graphical form in Fig 6 where the 3 bubbler phenolphthalin response is arbitrarily set at 1 to 1. The 3 bubbler system represents complete capture of ozone as shown by negligible color developed in the third bubbler. It is convenient in atmospheric sampling to use a single bubbler even at the expense of some loss of oxidant. However, there appears to be a constant ratio between the 2 systems so that the 1 bubbler data can be converted to the 3 bubbler. The ratio of the single bubbler, phenolphthalin response to 2% potassium iodide, is pertinent to this study and the value of 2.62 was obtained and entered in line 2, Table I.

Finally, in the laboratories in the Armour Research Foundation, as a part of a research project supported by the Air Pollution Foundation, the response of phenolphthalin and 4% potassium iodide[10] to ozone was studied. In this case, Armour used the technique of quantitatively diluting a known high concentration of ozone to the ppm. range for the development of the response curves shown in Fig. 7. The technique involves starting with liquid ozone, pumping to get rid of oxygen, evaporating ozone into containers of known vol. of several cc. to an accurately measured pressure and using the gas laws to calculate the ozone amount. This method needs further development so that their results are to be considered preliminary. The ratios thus determined are entered in Table I.

It can easily be seen from Table I that the laboratory calibrations leave something to be desired in regard to consistency of phenolphthalin behavior. We have had to be arbitrary in establishing the correction factor for reducing the phenolphthalin oxidant data to the same basis on the other methods. We have settled on the value of 2 for the ratio of phenolphthalin to 2% KI response, and have so treated the data shown in this study. Unfortunately the details of ozone and hydrogen peroxide reaction with phenolphthalin are lacking and we have no good theoretical basis for the selection of this ratio. We note, however, that the

[9] Beatrice Levy. Phenolphthalin Method as a Measure of Ozone in the Atmosphere. Unpublished Rept. of Test No. D-40, Air Pollution Control District, Los Angeles County (Dec. 30, 1954).

[10] William Dupraw. A Tentative Chemical Method for Determining Ozone in the Atmosphere. Armour Research Foundation, prepared for Committee D-22, Amer. Soc. for Testing Materials (Feb. 1956).

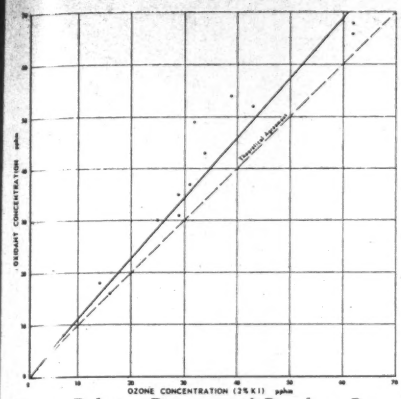

Fig. 8. Relative Response of Pasadena Potassium Iodide (20% Buffered) Oxidant Recorder. LACAPCD May 5, 1955.

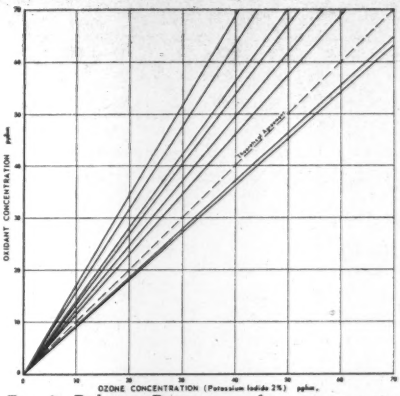

Fig. 9. Relative Responses of various continuous Oxidant Recorders (Potassium Iodide 20% Buffered). LACAPCD Mar.-July 1955.

literature states[11] that hydrogen peroxide reacts with phenolphthalin to produce phthalic acid and hydroquinone.

In the laboratories of the Air Pollution Control District relative response of the Beckman potassium iodide oxidant recorder and 2% potassium iodide unbuffered was studied. Fig. 8 shows the graph of the calibration data, the particular oxidant recorder used in obtaining the atmospheric oxidant of this study. A correction factor of 1/1.13 is indicated in order for these data to be on the same basis, namely to the 2% KI monitored ozone-in-air calibrating stream. In this case, the correction amounts to only 13%, Fig. 9 shows this factor may be as high as 70%.

The calibration of the ozone spectrometer is accomplished in the following way. The ozone concentration at time t is determined from the equation:

$$C_t = C_o + \frac{\log\left[\frac{I\lambda_{1,o}}{I\lambda_{2,o}} \cdot \frac{I\lambda_{2,t}}{I\lambda_{1,t}}\right]}{s(\alpha_1 - \alpha_2)}$$

Where

C_o = concentration of ozone at night when it is approximately O; say, 2 pphm.

$I\lambda_{1,o}$ = intensity of radiation at $\lambda_1 = 265$ $m\mu$ at same time as C_o is chosen.

$I\lambda_{2,o}$ = intensity of radiation at $\lambda_2 = 313$ $m\mu$ at same time as C_o is chosen.

$I\lambda_{1,t}$ = intensity at $\lambda_1 = 265$ at time t.

$I\lambda_{2,t}$ = intensity at $\lambda_2 = 313$ at time t.

$s = 325$ ft.

α_1 = absorption coefficient at $\lambda_1 = 265 = .123$ km^{-1} pphm.$^{-1}$

α_2 = absorption coefficient at $\lambda_2 = 313 = .001$ km^{-1} pphm.$^{-1}$

We have also used the ratio

$\frac{I\lambda_3}{I\lambda_1}$ where $\lambda_3 = 280$ $m\mu$.

Each day we read the ratio of the appropriate intensities when it reaches a minimum and set this as the condition for $C_o = 2$ pphm. This may occur as early as 10 PM or as late as 4 AM, or as in many cases the intensities fluctuate about a low value for several hours and we resort to an average minimum. For the rest of the day we associate the change in this ratio to the increase in ozone concentration by the above formula. Footnote 12 is the source of data for the absorption coefficients.

The above manipulations then presumably put both data on the same basis, namely responses are referred to dynamic calibrations with ozone-in-air streams which in time have been monitored with 2% KI. Since the rubber stock is also calibrated against ozone measured by iodine release from 2% KI, the 3 chemical systems are all referred to the same basis. Details of the ozone concentration calibrations used by spectroscopists in establishing the basic absorption data are not available. However, close agreement among the various investigators for the absorption coefficient implies good reproducibility in measuring ozone concentration in their absorption cells over a large range of values.

[11] Max H. Hubacher. *J. Amer. Chem. Soc.* **6**, 2097 (1943).

[12] Ernest Vigroux. Spectrophotometry-Absorption of Ozone at 18° below 3130A. *Compt. rend.* **234**, 2529-30 (1952).

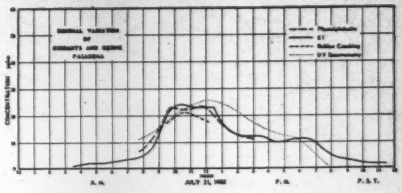

Fig. 10-A

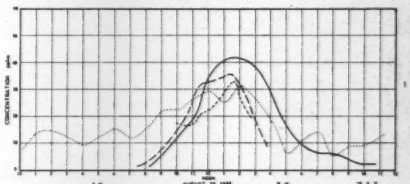

Fig. 10-B

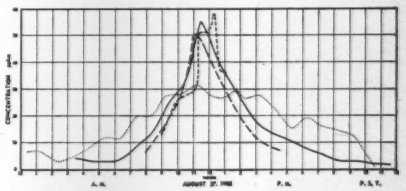

Fig. 10-C

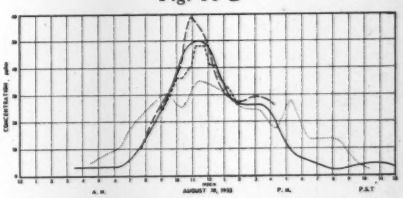

Fig. 10-D

Discussion of the Data

The results of sampling the atmosphere for the period, from July 15 to November 15, 1955, are summarized in graphical forms in Fig. 10-13. The phenolphthalin and potassium iodide oxidant data have been adjusted in accordance with the findings of the previous section.

Fig. 10 shows the diurnal variations of the responses of the 4 instruments for 4 typical smog days. The characteristic sharp increase in the early morning

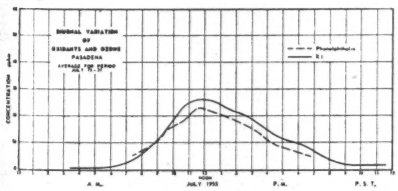

Fig. 11-A

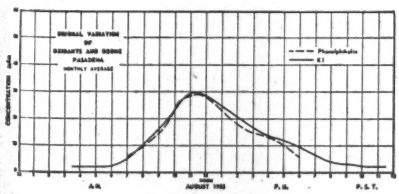

Fig. 11-B

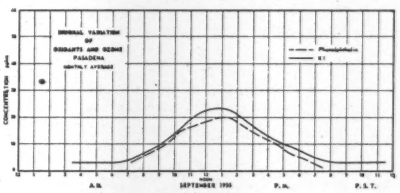

Fig. 11-C

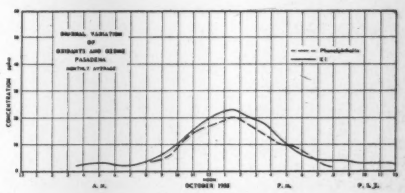

Fig. 11-D

hours rising to a peak in the middle of the day and gradual diminution in the afternoon are well demonstrated. Where meteorological factors were probably typical, there are double peaks or cases where a single peak occurs as early as 10 AM or as late as 3 PM.

The diurnal graphs indicate that the 3 chemical systems, phenolphthalin, potassium iodide, and rubber cracking, show the same response to smog oxidants both as regards shape of curves and concentration values. These are further demonstrated in Fig. 11 and 12 which show monthly and 4-monthly averages for phenolphthalin and potassium iodide. Since the number of sampling days and data are fewer for rubber cracking and spectrometry we have plotted those separately in Fig. 13. It should be noted that the spectrometer shows a flatter response than do any of the chemical systems, and ozone peak values are less. This might be due to the buildup of such other oxidants as organic peroxides, ozonides, and free radicals at the higher ozone concentrations. Since, as indicated in next section the oxidant nitrogen dioxide (NO_2) measured by the Saltzman reagent either decreases or remains fairly low in concentration during the day, it is not likely that this contaminant can account for the increase in oxidant over ozone. If sulfur dioxide is present in appreciable quantities the total oxidant would be larger than that indicated by the phenolphthalin or potassium iodide since SO_2 would depress their response. Reducing agents might also account for the oxidant reading being lower than ozone in early morning and late afternoon.

An indication of the order of magnitude of other oxidants can be computed from say the atmospheric phenolphthalin oxidant response. When this value is 100 pphm. and ozone is 30 pphm. of this total, one then multiplies the ozone value by 2 to relate it to peroxide calibration, then one obtains 100—60 or 40 pphm. of other oxidant. This would be a minimum value since peroxides of different kinds are known not to react quantitatively with phenolphthalin (*i.e.*, dialkyl peroxides do not react at all). Footnote 20 gives a result of 38 pphm. for peroxides in air using the peroxidase test.

Discussion of Interferences

Cholak[13] has carried out laboratory experiments on the effect of two air contaminants of interest to this study, nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) upon oxidant measurement by potassium iodide (20% buffered.)

Cholak concludes that the response of the oxidant recorder is 1 part oxidant to 5 parts nitrogen dioxide using ozone as the oxidant. Since recent data indicates[14] average nitrogen dioxide concentrations of the order of 5-15 pphm. during the middle of the day, corrections of 1 to 3 pphm. should be applied to potassium iodide oxidant data.

Cholak's results of the effect of sulfur dioxide were more serious with 3 pphm. SO_2 causing a reduction of 1 pphm. of recorded oxidant (ozone). Unfortunately, we have no data for SO_2 concentration for Pasadena. However, if we examine some 1954 data for downtown Los Angeles, we note SO_2 reached a peak of 10 pphm. based on the 4 mo. average. The 4-mo. average oxidant for this same sampling station reached a peak of 13 pphm. Based on the above results the corrected oxidant would have been 16 pphm. We would expect similar conditions to obtain in Pasadena unless there were an additional effect of a local source of SO_2.

Levy[15] has carried out similar laboratory studies of the effect of NO_2 and SO_2 on phenolphthalin. The results indicate 80 pphm. of NO_2 would give the same response as 12 pphm. of ozone. Therefore, in the atmospheric phenolphthalin oxidant data the effect of 5 to 15 pphm. of NO_2 would be less than 2 pphm. of oxidant. The results with SO_2 were such that the effects were smaller than the probable error in oxidant measurement itself, *i.e.* up to 50 pphm. SO_2 gives 1 or 2 pphm. reduction of oxidant.

Haagen-Smit[6] has studied the effects of NO_2 and SO_2 on rubber cracking. For both contaminants he finds negligible effects for the low concentrations (0-100 pphm.) involved. However, Crabtree[16] has observed that stressed rubber is cracked in a manner indistinguishable from ozone by the free radicals; tertiary butoxy, phenyl, benzoyl, acetyl, and hydroxyl. Since these radicals may be produced by the catalyzed photolysis of volatile peroxides assumed in smog, they could be considered a possible interference to ozone by rubber cracking method.

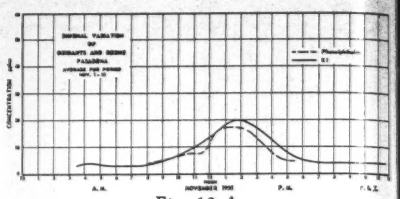
Fig. 12-A

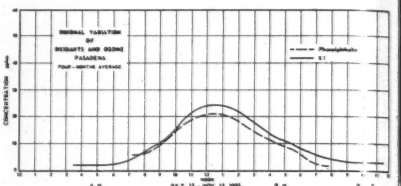
Fig. 12-B

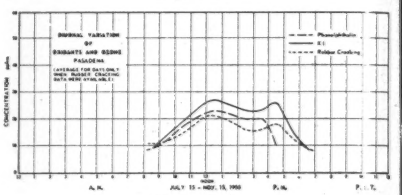
Fig. 13-A

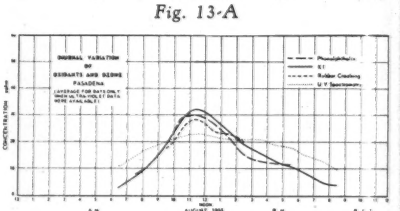
Fig. 13-B

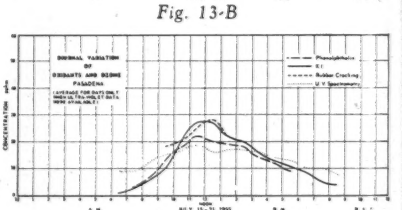
Fig. 13-C

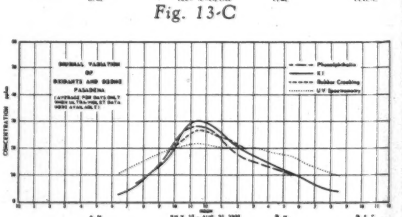
Fig. 13-D

Brattain[17] in reviewing the possible interferences to ozone determination by ultraviolet spectrometry by using the ratio $\frac{I_{265}}{I_{313}}$ states the following substances would be important; napthalene, 1 and 2 methyl napthalene, anthracene, phenanthracene, benzoyl peroxide and pyridine. To a lesser extent cyclopentadiene, toluene, and p-xylene would also inter-

[13] J. Cholak, L. J. Schafer, W. J. Younker and D. Yeager. Air Pollution in a Number of American Cities. *A.M.A. Arch. Ind. Health* 11, 280-9 (April 1955).

[20] Haagen-Smit, A. J. Chemistry and Physiology of Los Angeles Smog *Ind. & Eng. Chem.* 44, 1342-46, (June 1952).

[14] Air Pollution Foundation and Los Angeles County Air Pollution Control District, Unpublished data on Concentrations of NO and NO_2 in Los Angeles Atmosphere 1955.

[15] Beatrice Levy. Evaluation of the Interference of NO_2 and SO_2 in the Measurement of Ozone by the Phenolphthalin Method. Unpublished Report of Test No. D-8, Air Pollution Control District, Los Angeles County (July 1, 1954).

[6] See footnote 6, page 155.

[16] Crabtree, J. and Biggs, B. S. Cracking of Stressed Rubber by Free Radicals *J. Polymer Sci.*, 11, 280-1 (1953).

[17] Brattain, R. Personal communication to N. A. Renzetti.

fere. However, use of the additional ratio $\frac{I_{280}}{I_{265}}$ for the ozone determination would minimize the possible effect of the above substances. Furthermore, additional data from infrared spectrometry on the concentrations of hydrocarbons in the Pasadena atmosphere indicate[2] that these reach a maximum when oxidant concentration is low and vice versa.

Other possible interference in this method is that due to selective attenuation by particulate scattering of the radiation at the wavelengths used. Fortunately some data by Baum and Dunkelman[18] show that over the visual range 0.4 to 12 miles, errors corresponding to 1 or 2 pphm. of ozone only can develop. It should be noted that the effect of all of the interferences discussed for the spectrometric method would make the ozone determinations as presented in this report higher than the true ozone concentration in the atmosphere.

Conclusions

The response of potassium iodide and rubber cracking to Los Angeles smog in Pasadena are essentially the same when their calibrations are derived by an ozone-in-air stream. The response of phenolphthalin is also the same if definitive laboratory calibrations with ozone establish the ratio of 2 for phenolphthalin to 2% potassium iodide as used in this study.

These chemical systems respond to other oxidants in addition to ozone in the smog as judged by the ozone concentrations derived from ultraviolet absorption spectrometry.

These other oxidants reach 10-40 pphm. concentrations for ozone values above 20 pphm.

When the reagent phenolphthalin calibrated with H_2O_2 is used as an indicator of ozone concentration, a correction factor should be established empirically for the particular instrumental arrangement used in sampling. It is expected that this factor will lie between 2 and 3.

Recommendations

Since phenolphthalin, potassium iodide, and rubber cracking show essentially the same response on the average, any one can be used as an indicator of oxidant in Los Angeles smog provided that a common reference method is used for their calibrations.

An oxidant recorder not responsive to ozone should be used to monitor smog in order to establish its correlation with eye irritation and plant damage. Footnotes 19 and 20 suggest 2 techniques applicable to this problem.

Additional comparative studies at other locations in the Los Angeles Basin should be undertaken to see if similar relations between oxidants and ozone are obtained. For example, different relations might indicate different stages of the smog-forming reactions.

Either spectroscopic apparatus or 2% KI should be used for calibrating ozone-in-air streams which in turn are to be used for the calibration of other ozone or oxidant methods in the range of concentration 0-100 pphm.

Sufficient laboratory response studies should be conducted to eliminate lack of consistency in the results from previous investigations.

Acknowledgments

We wish to express our appreciation to Professor A. J. Haagen-Smit of California Institute of Technology and M. M. Fox, Air Pollution Control District for their phenolphthalin oxidant data and advice on interpretation; to Dr. L. H. Rogers, Air Pollution Foundation and Dr. Paul Mader, Air Pollution Control District for helpful conversations; to the Rock Island Arsenal, Army Ordnance Department for the loan of some components of the ozone spectrometer; California State Department of Health for making their data available to us; to the Data Reduction Group, Air Pollution Control District and Rita Tice, Air Pollution Foundation for their painstaking labor on data processing; to the Field Group of Air Pollution Control District and E. M. Liston, Air Pollution Foundation for the operation of various recorders.

[2] See footnote 2, page 154.

[18] Baum, William A. and Dunkelman, L. Horizontal Attenuation of Ultraviolet Light by the Lower Atmosphere. *J. Opt. Soc. Amer.* **45**, 166-75 (1955).

[19] Todd, Glenn W., Modification of Ferrous Thiocyanate Colorimetric Method for Determination of Some Atmospheric Oxidants, *Anal. Chem.* **27**, 1490-92 (Sept. 1955).

[20] See footnote 20, page 158.

Recent Developments in the Study of the Organic Chemistry of the Atmosphere*

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Traditionally air pollution is thought to arise when excessive amounts of harmful or irritating substances are discharged into the atmosphere. This is the case in many air-pollution problems. The pollutants discharged into the air are in themselves objectionable, whether they are gaseous substances or solid particles such as comprise smoke. When the air is stagnant so they can accumulate, a serious situation may develop.

In some circumstances the situation may be further complicated by reactions occuring between different pollutants, or between pollutants and the natural constituents of the air. This has made the study of the Los Angeles smog difficult. Principal sources of air pollution in the Los Angeles area are motor-vehicle exhaust, rubbish incineration, and industry. However, the mixture of contaminants discharged into the atmosphere undergoes a complex series of reactions when irradiated with sunlight; it forms products much more objectionable than the materials originally discharged into the air. These products damage crops, irritate eyes, and lead to the formation of an aerosol reducing visibility. In spite of years of study, the compounds responsible for these effects have not been unambiguously identified. It has, however, become apparent that photochemical reactions of organic materials combined with nitrogen dioxide and ozone play key roles in the development of smog of the Los Angeles type. In May 1953 a program to study these reactions was started at the laboratories of The Franklin Institute under the sponsorship of the Smoke and Fumes Committee of the American Petroleum Institute.

The First Experiments

The prime difficulty in any program of this nature lies in obtaining selective analytical methods. To obtain reliable results, the methods used must permit unequivocal identification of particular compounds in the presence of an unknown mixture of other compounds. Infrared absorption can provide necessary selectivity, but ordinary equipment does not have nearly enough sensitivity to detect substances at low concentrations of smog. Accordingly, first experiments were done with concentrations of reactants many times higher than are ever found in polluted air. These results were summarized in a paper presented last

* Presented to a session on smoke and fumes, at the 21st Midyear Meeting, the American Petroleum Institute's Division of Refining, Sheraton-Mount Royal Hotel, Montreal, Que., Canada, May 16, 1956.

year at the 20th Midyear Meeting of the Division of Refining.[1]

In these experiments either nitrogen dioxide or ozone was mixed with an organic compound at concentrations of about 1 part/thousand in air or oxygen and allowed to react with or without artificial sunlight; the products were analyzed by means of standard infrared techniques. Alkyl nitrate, alkyl nitrite, aldehyde, and peroxyacid were typical products of the nitrogen-dioxide—organic-compound reaction.

Ozone, which has played a central role in studies of the Los Angeles smog, was not detected as a product in this first study. Ozone was found to react slowly with saturated hydrocarbons but rapidly with olefins. Peroxyacids were identified among the products when ozone was reacted with aldehydes.

During these first studies it became obvious it would be desirable to study these reactions at concentrations nearer to those encountered in polluted air. This required design and construction of a special reaction vessel and infrared absorption cell. This cell utilized a multiple-reflection system of the White type. By adjustment of the 2 mirrors at the right-hand end of the cell shown in Fig. 1, it is possible to obtain any integral multiple of 4 passes through the cell. Inasmuch as the mirrors at the right end are 3 m. from the smaller mirror at the left end, 144 passes through the cell gives a total path length of 432 m. Since infrared paths of approximately 500 m. could be obtained, it was possible to detect reaction products at concentrations of a few tenths of a ppm.

In the first experimental program carried out with this cell, ozone as a product was found in concentrations of 1 ppm. to 2 ppm. and less when nitrogen dioxide and various organic compounds were reacted. In these experiments reactants at a few ppm. in oxygen or air were irradiated with an AH-6 arc enclosed in pyrex as shown in Fig. 1. The variation of ozone concentration with time of irradiation was found to depend, in a complex way, on structure of the organic compound and on the concentration of both reactants. The transitory formation of ozone by the photolysis of nitrogen dioxide in oxygen was demonstrated; it was shown if the fast back reaction between ozone and nitric oxide is suppressed by the addition of nitrogen pentoxide to react with the nitric oxide, the ozone will quickly accumulate in the

[1] P. L. Hanst, E. R. Stephens, and W. E. Scott. Reactions Involving Ozone, Nitrogen Dioxide, and Organic Compounds at Low Concentration in Air. *Proc. API* 35 [III] 175-87 (1955). Also J. of APCA February 1956. 5, 219 (1956).

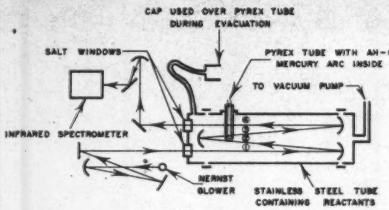

CAP USED OVER PYREX TUBE DURING EVACUATION
SALT WINDOWS
PYREX TUBE WITH AH-6 MERCURY ARC INSIDE
TO VACUUM PUMP
INFRARED SPECTROMETER
NERNST GLOWER
STAINLESS STEEL TUBE CONTAINING REACTANTS

Fig. 1. Long-path infrared absorption cell.

system. The results of this study were reported to the American Chemical Society in September 1955.[2]

Other products observed in this first study with the long-path cell were aldehyde, alkyl nitrate, formic acid, carbon monoxide, carbon dioxide, and water. Several prominent absorptions which apparently all belong to one compound could not be identified. This interesting product, referred to as compound X, has been subjected to considerable study in an attempt to determine its structure and physical properties. Aside from ozone, it is probably the most important product of these reactions.

Compound X

Obtaining samples of compound X for study presented some difficulty. When organic compounds and nitrogen dioxide are photolyzed at high concentrations (on the order of mm. of mercury), alkyl nitrate is the chief nitrogen-containing product and compound X is not formed. The only successful technique of preparation of compound X which has been found is actual photolysis of mixtures of organic compounds and nitrogen dioxide at low pressures in the presence of oxygen. Diacetyl was found to give the best results; *i.e.* it gave least amount of side products. With 100 ppm. each of diacetyl and nitrogen dioxide in 1 atm. of oxygen, about 2 hr. of AH-6-arc irradiation was found to be necessary for most of the reactants to be converted to products. At these low pressures of reactants a large volume of gas was required in order to give enough compound X for a liquid sample to be collected. Therefore, the reaction was conducted in the 500-*l.* long-path absorption cell. At the end of the reaction products were slowly pulled through a trap cooled by a dry-ice-*iso*propyl-alcohol mixture. This trap passed some of the products, such as acetaldehyde, carbon dioxide, and carbon monoxide, but it trapped the compound X—or at least part of it. It also trapped water vapor and some unreacted diacetyl. However, an infrared spectrum, a mass spectrum, and a nuclear magnetic-resonance spectrum of the compound were obtained, and it was possible to perform qualitative tests of its chemical properties.

[2] E. R. Stephens, P. L. Hanst, R. C. Doerr, and W. E. Scott. Reactions of NO_2 and Organic Compounds in Air at Concentrations of PPM. Paper presented to the 128th National Meeting of the American Chemical Soc., Minneapolis, Minn., Sept. (1955). Ind. & Eng. Chem. 48, 1498 (1956).

The infrared spectrum of the compound X from diacetyl is shown in Fig. 2. It shows the following features:

1. The CH absorption is weak compared to other strong bands in the spectrum, indicating a methyl compound.
2. There is a strong single carbonyl band at 5.75 μ similar in shape and wave length to the carbonyl bands of aldehydes, ketones, peroxyacids, and esters, and different from the double carbonyl bands of acids, acid anhydrides, and diacyl peroxides. There is a neighboring, weaker band at 5.4 μ which might be considered a part of a double carbonyl band, but this seems doubtful because the 2 branches of a double carbonyl band are usually of approximately equal intensity and are usually closer together. The indications are that compound X from diacetyl is an acetyl compound—a very logical product.
3. The bands at 5.4 μ, 7.7 μ and 12.6 μ indicate presence of nitrogen in the molecule for the following reasons:
   a. Bands near 5.4 μ arise from the nitricoxide stretching vibration in nitric oxide, nitrosyl chloride, and nitrogen tetroxide; few other compounds have bands here.
   b. Alkyl nitrates, nitroso compounds, and nitrogen tetroxide absorb near 7.7 μ.
   c. Alkyl nitrites have a strong band near 12.6 μ which is supposed to originate in the nitric-oxide group.
4. There is a particularly strong band in the spectrum which had not previously been assigned to compound X. This is the band at 8.6 μ. Identification of the band at 8.6 μ was important because it was the only major unidentified band in the spectra of the reaction products from organic compounds and nitrogen dioxide, other than the bands which were obviously due to compound X. This band, unlike the bands at 5.4 μ, 5.74 μ, 7.7 μ, and 12.6 μ, appears in the spectrum of the sample of compound X prepared from diacetyl but not in

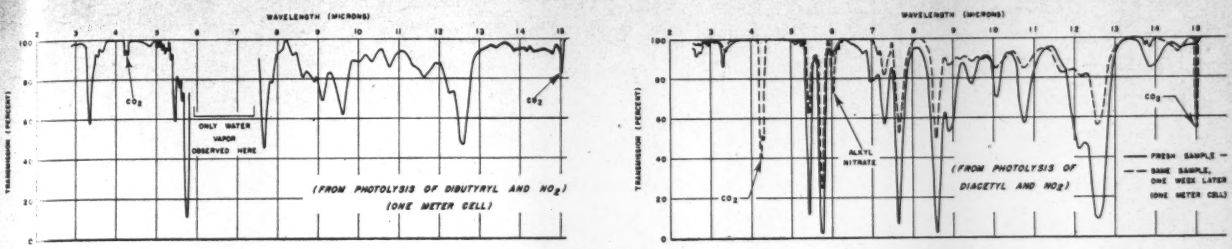


Fig. 2. Infrared spectrum of Compound X prepared from diketones.

a sample prepared from dibutyryl (Fig. 2). Thus compound X is probably really a homologous series of compounds of which only the lowest member possesses a band at 8.6 μ. The products of the reaction of nitrogen dioxide with 2-pentene or with methylethyl ketone also showed this band.[2] The sample prepared from dibutyryl also has a moderate-strength band at 9.6 μ which had been observed in the spectra of reaction products.

The mass spectrum of a gaseous sample of compound X from diacetyl was recorded. The main peaks are listed in Table I. The highest mass peak, 86, almost certainly arose from diacetyl impurity. This identification is corroborated by the 87 peak which is nearly the right height to be an isotope peak for a 4-carbon molecule. The very strong peak at one half this mass, 43, cannot result entirely from diacetyl. Nor can it result from acetic acid, the presence of which is indicated by peaks at mass 60 and mass 45 which are in the proper intensity ratio. Thus the presence of an acetyl radical in compound X is indicated. In addition, there are peaks at 46 and 30 most probably arising from the nitrogen-dioxide fragment and the nitric-oxide fragment, respectively. This indicates that compound X is an acylnitrogen compound. The carbon dioxide indicated by the peaks at mass 44 and mass 22 (again having the proper intensity ratio) may well have arisen in the decomposition of compound X and may not have been present, as such, in the original sample. The peak at 61 probably arose from methyl nitrite. It is believed that this may have been formed, along with carbon dioxide, as a product of the decomposition of compound X. This decomposition could have occurred in the inlet system of the spectrometer. The peaks at 72 and 71 seem to be clearly associated with compound X since none of the compounds known to be present —diacetyl, acetic acid, or methyl nitrite —gives a peak at this mass/charge ratio.

[2] See footnote 2, page 160.

The proton region of the nuclear magnetic-resonance spectrum of the compound X formed from diacetyl, nitrogen dioxide, and oxygen was recorded through the courtesy of Esso Research Laboratories. It showed there is only one type of hydrogen present in the molecule.

The decomposition products of compound X were examined for clues to its structure. In one experiment a sample was allowed to decompose for over a week at room temperature in oxygen. The infrared spectrum (Fig. 2) of the products showed carbon dioxide and a small amount of organic nitrate. It is clear from this the original molecule contained nitrogen. The surprising weakness of the product spectrum led to the suggestion that adsorption on the cell walls was occurring rather than decomposition. But the marked increase in carbon-dioxide concentration argues against this. There was no nitrous oxide, nitric oxide, nitrogen dioxide, nitrogen pentoxide, nitrous acid, nitric acid, nitrite, or nitro compound evident. In another experiment compound X was decomposed by heating in nitrogen at 185°C. for 2 hr. The spectrum of the products of this reaction showed small amounts of carbon dioxide, carbon monoxide, formaldehyde, methyl alcohol,

TABLE I

Mass Spectrum of Gaseous Sample of Compound X

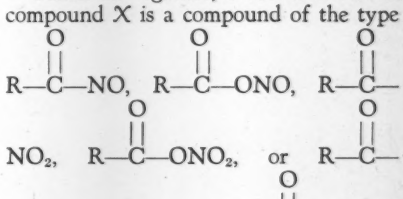
Mass/ Charge Ratio	Peak Ht.	Mass/ Charge Ratio	Peak Ht.	Mass/ Charge Ratio	Peak Ht.
91	0.4	53	8.1	36	4.1
87	7.7	52	2.3	32	59.5
86	166	51	3.7	31	69
77	0.5	50	9.0	30	780
76	1.5	49	5.4	29	252
72	5.8	48	11.5	28	298
71	1.8	47	8.5	27	45
64	12	46	280	26	48
62	1.8	45	400	25	27
61	20.5	44	775	24	9
60	206	43	2,550	22	11.8
59	1.0	42	217	18	760
58	10.5	41	71	17	265
57	8.0	40	17	16	195
56	6.9	39	13.8	15	1,060
55	4.0	38	9.5	14	420
54	2.5	37	12.1	13	138
				12	110

probably nitromethane, and methyl nitrite. There was no nitrous oxide, nitric oxide, nitrogen dioxide, nitrogen pentoxide, nitrous acid, nitric acid, or nitrate evident. Unfortunately, it has not been possible to draw many conclusions from these products, although they do indicate again that nitrogen is present in the molecule. On one occasion a 2-drop sample of compound X exploded with extreme violence, again showing this compound's instability.

Compound X dissolves in water, probably hydrolyzing, to form a strongly acid solution which can act as either an oxidizing agent or a reducing agent; i.e. it liberates iodine from potassium-iodide solution, and it decolorizes potassium permanganate. The solution gives the *brown ring* test for nitrite and nitrate. When a few drops of compound X were mixed with a few drops of water, and the mixture was evaporated back into the long-path cell, the spectrum showed nitric acid had been formed.

An important property of compound X is its rapid production of ozone when photolyzed in oxygen. This will be discussed subsequently, but it is appropriate to mention the only other compounds found to produce ozone readily on photolysis are the nitrites. In its ozone-producing properties compound X behaves like a nitrite.

Taken all together, evidence indicates compound X is a compound of the type



OONO. The formula R—C(=O)—OONO, which could be called peroxyacyl nitrite, appears to be the most likely. Such a compound seems likely to have all the observed physical and chemical properties of compound X, and a mechanism for its formation can easily be written down, as follows:

1. Acyl radicals are produced in photolysis of diacetyl or when

hydrogen is abstrated from aldehyde, or when an oxygen atom or an ozone molecule reacts with olefin.

2. The acyl radicals add oxygen to give the peroxyacyl radical $R-\overset{\overset{O}{\|}}{C}-O-O$. This reaction seems probable because, at the concentrations at which compound X is formed, the acyl radical collides with oxygen several thousand times more frequently than with any of the other possible reactants. The likelihood of the reaction is also indicated by the fact the low-temperature oxidation of aldehyde in pure oxygen produces peroxyacids.

3. The peroxyacyl radical adds nitric oxide to produce $R-\overset{\overset{O}{\|}}{C}-O-O-NO$. This is consistent with the fact that nitric oxide is itself a free radical with an unpaired electron and is commonly used as an inhibitor of free radical reactions.

Whatever the exact formula of compound X, it is obvious it contains nitrogen, and it is likely that it is formed in the reaction between a free radical and nitric oxide. It appears to be the key to the understanding of many of the observed facts, as will be pointed out in subsequent paragraphs.

Mechanism of Ozone Formation

The identification of compound X as an acyl-nitrogen compound fits in with observed facts of ozone formation in nitrogen - dioxide - organic - compound photochemical reactions. A summary of the mechanism follows.

First, photolysis in the absence of organic material is considered, based on data presented in a previous paper.[2] Nitrogen dioxide is photolyzed by the ultraviolet radiation present in sunlight:

$$NO_2 \xrightarrow{h\nu} NO + O$$

The oxygen atom so produced reacts with an oxygen molecule:

$$O + O_2 \rightarrow O_3$$

In the absence of an organic material this ozone reacts quickly with the nitric oxide produced by the photodissociation,

$$NO + O_3 \rightarrow NO_2 + O_2,$$

preventing accumulation of a significant amount of ozone. These three reactions predict equal steady-state concentrations of ozone and nitric oxide will be formed when nitrogen dioxide in oxygen is irradiated with ultraviolet radiation (assuming the steady-state concentration of atomic oxygen is insignificant). Actually, the ozone formed under these circumstances is observed to disappear under continued irradiation, and it appears nitric oxide accumulates in the system. This is ascribed to the occurrence of a slower side reaction which either produces nitric oxide or consumes ozone. A good possibility is:

$$O + NO_2 \rightarrow NO + O_2$$

It was predicted if some other reactant was introduced into the system to remove nitric oxide in competition with the ozone-nitric-oxide reaction, the ozone would accumulate. Nitrogen pentoxide was found to produce the predicted effect; photolysis of the nitrogen - dioxide — nitrogen - pentoxide—oxygen system yielded substantial quantites of ozone.

When nitrogen dioxide is photolyzed in the presence of an organic substance (in oxygen), free radicals arising during the oxidation of the organic material are believed to play a part similar to the nitrogen pentoxide. That is, they react with the nitric oxide to form compound X allowing ozone to accumulate in the system. This mechanism readily accounts for the parallelism between the rate of compound X formation, the rate of ozone formation, and the rate of nitrogen-dioxide disappearance which was reported in the previous paper.[2] The mechanism also explains the fact that photolysis of nitrogen-dioxide—organic-compound—air mixture sometimes produces ozone concentration in excess of the initial nitrogen-dioxide concentration. The reason for this is that compound X is photolyzed in air to produce ozone (discussed hereinafter). In this reaction nitrogen dioxide is probably first formed and is then quickly photolyzed, leading to ozone and probably to regeneration of compound X.

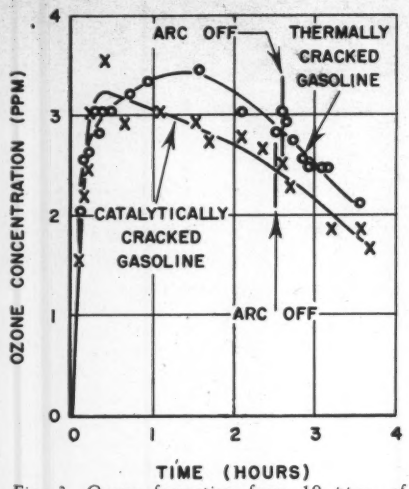


Fig. 3. Ozone formation from 10 ppm. of gasoline, 5 ppm. of nitrogen dioxide, and 1 atm. of oxygen.

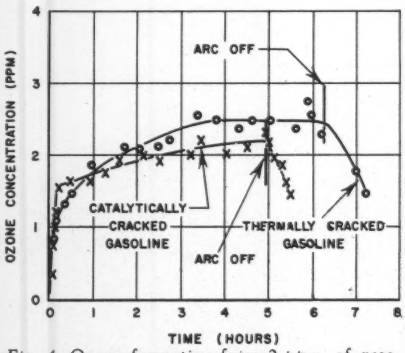


Fig. 4. Ozone formation from 2 ppm. of gasoline, 1 ppm. of nitrogen dioxide, and 1 atm. of oxygen.

The chain oxidation of the organic material presumably is initiated by the attack of an oxygen atom on an organic molecule. There are a number of ways each oxygen atom used in this initial attack may lead to the formation of many free radicals capable of reacting with nitric oxide. These are chain-branching during oxidation; photolysis of intermediates formed during oxidation, such as aldheydes; and photolysis of compound X itself. For this reason only a fraction of the oxygen atoms produced by the photolysis of nitrogen dioxide are consumed in initiation reactions, while the majority react with molecular oxygen to form ozone.

The observation made by Haagen-Smit and Fox,[3] and confirmed by long-path cell studies,[2] that there is an upper-limit concentration of nitrogen dioxide above which ozone is not produced within a limited irradiation time is readily explained. With a high initial concentration of nitrogen dioxide, photolysis produces nitric oxide more rapidly than it can be consumed by free radicals produced from the organic material. With continued irradiation, the rate of formation of nitric oxide is slowed down because nitrogen dioxide is depleted. The free radicals then slowly consume nitric oxide to form compound X, eventually reducing the nitric-oxide concentration sufficiently to allow ozone to accumulate. This delay in formation of ozone was observed in studies with the long-path cell. It was also observed the limiting concentration of nitrogen dioxide is reduced by increasing the initial hydrocarbon concentration. This is explained by the fact that, with greater hydrocarbon concentration, capacity to consume nitric oxide by the free-radical mechanism is increased.

[2] See footnote 2, page 160.

[3] A. J. Haagen-Smit and M. M. Fox. Automobile Exhaust and Ozone Formation, *SAE Trans.* **63**, 575-580 (1955).

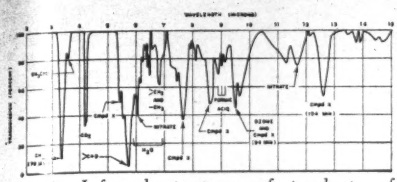


Fig. 5. Infrared spectrum of products of photolysis of 10 ppm. of thermally cracked gasoline and 5 ppm. of nitrogen dioxide in 1 atm. of dry oxygen; path = 240 m.

Ozone from Gasoline—Nitrogen-Dioxide Mixtures

A study has been made of the ozone-forming properties of gasoline-nitrogen-dioxide mixtures in air. Two gasoline samples were obtained. They are debutanized full-range gasoline blends; one comprises only catalytically cracked fractions and the other only thermally cracked fractions, each sample blended in typical production proportions. Each sample was studied at 2 different concentrations in the ppm. range with a 2 fold excess of gasoline over nitrogen dioxide. The gasoline was placed in the reaction cell by totally vaporizing a few drops in a small bulb and then using as much of this vapor as was desired. This was done in order to avoid the change in composition which could result if a small sample were vaporized from a large volume of liquid. The ozone formation is shown in Fig. 3 and 4.

The graphs show no appreciable difference in either the amount of ozone formed or the rates of ozone formation. A striking result of the experiments is that when the concentration of reactants was reduced fivefold, the maximum amount of ozone formed was reduced by only one third. Another important result is that when 2 ppm. of gasoline and 1 ppm. of nitrogen dioxide were photolyzed, the maximum concentration of ozone formed was more than twice the starting concentration of nitrogen dioxide. This is evidence if the ozone is produced by the nitrogen-dioxide photolysis mechanism already outlined herein, there must be a mechanism for reoxidizing nitric oxide to nitrogen dioxide without consumption of ozone. Such a mechanism is provided by the formation of compound X and its photolysis to yield nitrogen dioxide.

The nitrogen dioxide disappeared quickly in these experiments, just as it did in the studies of ozone production from pure olefins which were previously reported. Also, compound X formed quickly, and its formation coincided with the nitrogen-dioxide disappearance. The spectrum of the products of the reaction of 10 ppm. of thermally cracked gasoline and 5 ppm. of nitrogen dioxide in oxygen is shown in Fig. 5. The principal products (besides water, carbon dioxide, and carbon monoxide) were ozone, compound X, and formic acid. Lesser amounts of aldehyde and alkyl nitrate were evident. The catalytically cracked gasoline also gave these products.

Measurements of the concentration of reactants and products were made by scanning characteristic absorption bands at various times during the irradiation. The following behavior was observed for both gasoline samples:

1. After the initial fast disappearance of nitrogen dioxide, none was detected during the remainder of the experiment.
2. The ozone concentration increased rapidly as the nitrogen dioxide disappeared; in the reactions at the lower pressures it continued to increase slowly long after the nitrogen dioxide was gone.
3. The compound X built up fast and then fell off slowly during the remainder of the reaction.
4. The hydrocarbon CH band changed shape quickly at first and then slowly diminished during the remainder of the time.
5. When the irradiation was stopped in the lower-concentration experiments, the ozone concentration dropped quickly.

These observations suggested the following:

After the initial nitrogen-dioxide photolysis and associated ozone formation, some product was slowly photolyzed to produce additional ozone. It is possible this slowly photolyzing product was being regenerated, and if irradiation had been continued long enough, ozone production would have continued until all hydrocarbon was reduced to smaller,

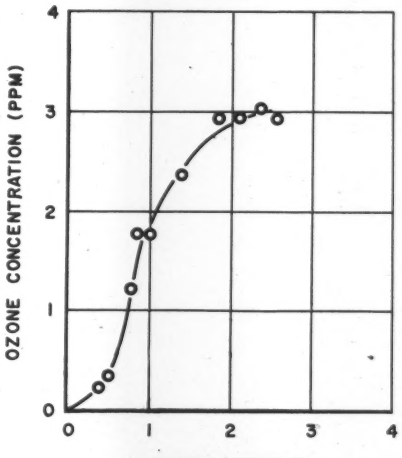


Fig. 7. Compound X prepared from diacetyl and nitrogen dioxide. Ozone formation from 6 ppm. of catalytically cracked gasoline, a few ppm. of Compound X, and 1 atm. of oxygen.

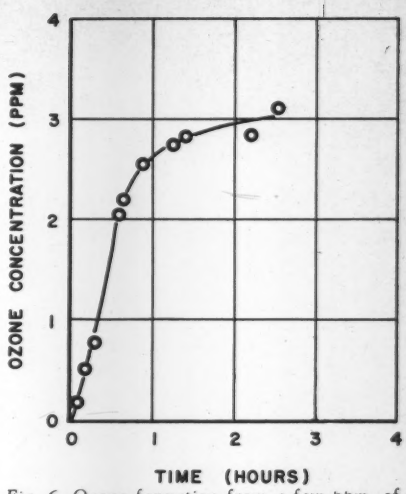


Fig. 6. Ozone formation from a few ppm. of Compound X and 1 atm. oxygen.

more inert substances such as methane, formic acid, formaldehyde, carbon dioxide, carbon monoxide, and water. This photolyzable product is believed to be compound X.

Photolysis of Compound X, Butyl Nitrite, and Diacetyl

A relatively pure sample of compound X was prepared from diacetyl and nitrogen dioxide with use of the photolysis and cold-trap-collection technique previously described in this paper. This sample was then vaporized back into the long-path cell, mixed with 1 atm. of oxygen, and photolyzed with the AH-6 arc. The exact partial pressure of the compound X could not be measured because of the presence of an unknown percentage of water vapor. However, if the compound-X infrared bands are comparable in strength to those of nitrites and nitrates, its partial pressure was in the ppm. range. Ozone was quickly formed in the photolysis. This is shown in Fig. 6. The same amount of compound X in oxygen was then photolyzed in the presence of 6 ppm. of catalytically cracked gasoline. Ozone was again formed, but it was delayed, as is shown in Fig. 7. This delay was probably the result of the rapid reaction of the initially formed ozone with the olefins of the gasoline.

When photolyzed in oxygen, *n*btuyl nitrite was found to produce ozone readily. The rate of ozone production and the amount of ozone produced were comparable to the rate and amount observed in the photolysis of compound X.

Pure diacetyl, dibutyryl, or pyruvic acid have all been reported to produce ozone on photolysis in oxygen.[4] First

[4] A. J. Haagen-Smit, C. E. Bradley, and M. M. Fox. Ozone Formation in Photochemical Oxidation of Organic Substances. *Ind. Eng. Chem.* 45. [9] 2086-9 (1953).

attempts to verify this result with use of the long-path infrared technique were frustrated by appearance in the spectrum of a band of methyl alcohol which masked the absorption resulting from ozone. This difficulty was overcome by the use of the following technique:

1. The diacetyl was photolyzed, and the spectrum was recorded in the ozone-methyl-alcohol region (9 μ to 10 μ).
2. The ozone was removed by the addition of a relatively large amount of nitrogen dioxide.
3. The spectrum was again recorded.
4. The second spectrum was subtracted from the first.

The difference spectrum turned out to be a very good ozone spectrum. Sample *before* and *after* spectra, and their difference, are shown in Fig. 8. Three different concentrations of diacetyl were used, each in 1 atm. of dry oxygen. They were photolyzed 20 min. with the AH-6 arc, and then the spectra were recorded. The results were as shown in Table II.

The amount of water vapor present was found to have no important effect on the amount of ozone produced. The *dry* atmospheres in which the diacetyl was photolyzed undoubtedly contained traces of water vapor.

An attempt was made to detect ozone as a product of the photolysis of 20 ppm. of pyruvic acid in 1 atm. of oxygen. None was detected, though a few tenths of a ppm. of ozone would have produced an identifiable absoption band.

The amount of ozone formed in the photolysis of diacetyl is small compared to amounts formed by photolysis from compound X or *n*butyl nitrite. It is also small compared to amounts formed in reactions involving organic compounds and nitrogen dioxide. The ozone formation from diacetyl must be the result of reactions involving free radicals and oxygen. Perhaps the photolysis of the nitrogen-containing compound X or *n*butyl nitrite also produces ozone through a free-radical mechanism and the greater amount of ozone is formed because of the greater reactivity of the radicals. However, it is believed these compounds first yield nitrogen dioxide, which then is photolyzed to yield ozone.

The Role of Sulfur Dioxide

Several experiments were conducted in order to see if sulfur dioxide affects, or is affected by, the photochemical reaction of nitrogen dioxide with hydrocarbons in oxygen. In one experiment, 5 ppm. of sulfur dioxide was added to a mixture of 10 ppm. of catalytically-cracked gasoline and 5 ppm. of nitrogen dioxide in 1 atm. of oxygen. In a second trial, 1 ppm. of sulfur dioxide was added

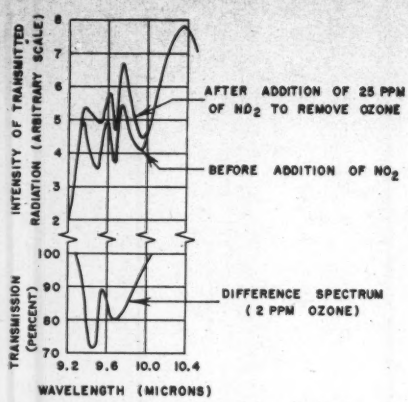


Fig. 8. Irradiation —20 min. with AH-6 arc. Infrared spectrum of ozone formed on photolysis of 50 ppm. of diacetyl in 1 atm of oxygen.

to a mixture of 2 ppm. of catalytically-cracked gasoline and 1 ppm. of nitrogen dioxide in 1 atm of oxygen. Results were compared to results of similar experiments previously conducted without sulfur dioxide. No pronounced effect on the ozone formation was observed. The ozone built up to about the same concentration in approximately the same length of time as in the previous experiments. However, in the experiments with sulfur dioxide added, ozone concentration decreased a little faster after the maximum. At the end of 1 hr. the amount of ozone was roughly the same as in previous experiments (3 ppm. for the 10-5-5 mixture and 1.7 ppm. for the 2-1-1 mixture), but at the end of 2 hr. it was roughly 20% lower in the experiments with added sulfur dioxide. This small change is not regarded as significant. The photolysis of a mixture of 10 ppm. of 2-pentene, 5 ppm. of nitrogen dioxide, 5 ppm. of sulfur dioxide, 10 mm. of mercury of water, and 1 atm. of oxygen produced about the same amount of ozone (3 ppm.) as a similar reaction without sulfur dioxide and water. Water, therefore, has little effect on the result. Another experiment showed sulfur dioxide has no effect on production of ozone in the photolysis of compound X.

The sulfur dioxide was found to be slowly reduced in concentration during these reactions. In the length of time required for the ozone to pass through its maximum, and for most of the products to be formed, sulfur dioxide was reduced in concentration by only a few per cent. Bands of sulfur trioxide at 7.5 and 8.9 μ were not observed.[5]

TABLE II

Ozone Formed by Photolysis of Diacetyl

Concentration of Diacetyl ppm.	Concentration of Ozone Produced in 20 Min. ppm.
50	2.0
25	0.9
10	0.4

Discussion

These experiments show ozone detected during a Los Angeles smog attack can be accounted for by photochemical reaction of nitrogen dioxide with organic compounds. It has been suggested the situation might be alleviated by reducing the amount of nitrogen oxides released into the atmosphere. It would be of interest to know whether ozone is produced directly from the nitrogen dioxide by the oxygen-atom mechanism outlined in this paper, or whether it is a byproduct of oxidation reactions such as the diacetyl-photolysis experiment described. The sum of evidence appears to favor the former mechanism. The amount of diacetyl necessary to produce a significant ozone concentration is considerably greater than the concentration of atmospheric contaminants. Furthermore, diacetyl is apparently in a class by itself in regard to ozone formation through photolysis if systems containing combined nitrogen are excluded.

Even on the basis of the mechanism involving the formation and photolysis of compound X, it would be hasty to conclude reduction in the amount of nitrogen oxides emitted into the atmosphere would proportionately reduce either the ozone concentration or smog severity (these 2 quantities are not necessarily directly proportional). The combined nitrogen may pass through this cycle many times, and may produce an ozone concentration not directly proportional to the initial nitrogen-dioxide concentration. The experiments with the 2 types of gasoline illustrate this point.

Future Plans

These laboratory studies of photochemical reactions demonstrated the ability of the long-path infrared absorption cell to provide positive identification of many common air contaminants at the low concentrations at which they occur in the atmosphere. Accordingly, a second instrument is being constructed to be used for direct analysis of the atmosphere. This second long-path cell will differ in only minor details from the first, but will be housed in a trailer and used for direct examination of polluted air. Experience gained in the laboratory studies has indicated a wide variety of common pollutants will be detectable and identifiable if present in concentra-

[5] H. Gerding and J. LeCompte. Infrared Absorption Spectrum of Sulfur Trioxide. *Nature* **142** [3598] 718 (1938).

tions on the order of 0.1 ppm. to 0.2 ppm. This list includes ozone, formic acid, acetylene, ethylene, higher olefins, acetic acid, acetone, aldehyde, compound X, and total hydrocarbon as CH. By removing water vapor it will probably be possible to determine nitrogen dioxide, sulfur dioxide, and other carbonyl compounds. One important gaseous contaminant which cannot be directly determined either before or after removal of water vapor is nitric oxide. It may be possible to devise a technique, perhaps involving oxidation of the nitric oxide to nitrogen dioxide, which will enable its determination.

Detection of compound X, in these laboratory studies, illustrates an important advantage of the infrared method of analysis over chemical methods. If compound X is formed in polluted air—and its prominence as a reaction product indicates that this is a strong possibility—its detection by chemical methods would be difficult. Furthermore, its chemical properties suggest it may interfere with the common analytical methods of air analysis, such as the potassium-iodide method for ozone.

Meanwhile, many problems yet unsolved can be attacked in the laboratory. The eye irritant present in the Los Angeles atmosphere has not been identified. The nature of the plant-damaging agent is still uncertain, although it is known typical smog damage can be produced by treating plants with products of the reaction of ozone with olefins. These problems and many others can and are being attacked with the long-path infrared cell.

Smog Effects and Chemical Analysis of the Los Angeles Atmosphere*

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Early in 1954, shortly after its formation, the Air Pollution Foundation entered into a contract with Los Angeles County to carry out an aerometic survey, or program of systematic measurement of selected pollutants and related variables in the atmosphere. About 2/3 of this large-scale sampling and analysis program was supported by public funds and the balance by private funds. The program included 24 separate projects and required the full-time or part-time participation of 305 persons for a total of over 9,000 man-days. Preliminary findings were reported at the Third National Air Pollution Symposium in Pasadena, Calif., April 18, 1955[1].

This paper reports additional interpretations of the data and summarizes correlations between smog manifestations as measured by its eye irritation, plant-damaging effects, and oxidant. A more complete report has been issued by the Air Pollution Foundation[2].

Los Angeles smog is now generally thought by the scientific workers on the problem to be in a part a result of photochemical oxidation reactions between organic matter and nitrogen oxides. These reactants are emitted by various human activities, and at times are trapped by meteorological and geographical conditions for a sufficient length of time to permit oxidation products to form to a degree where some of the reaction products give rise to the obnoxious effects associated with smog. The contribution of other contaminants, such as miscellaneous dusts, oxides of sulfur, lubricating oil mists, and halogenated solvents, may be important. Their significance is still to be determined.

Objectives

This survey was designed to (a) measure the distribution in severity and time of the various manifestations of smog; (b) establish relationships between the concentrations of various contaminants and manifestations of smog, the eye irritation, *viz.* plant damage, and reduced visibility; (c) ascertain patterns with respect to the movement of air pollution; and (d) observe trends in concentration changes of various contaminants.

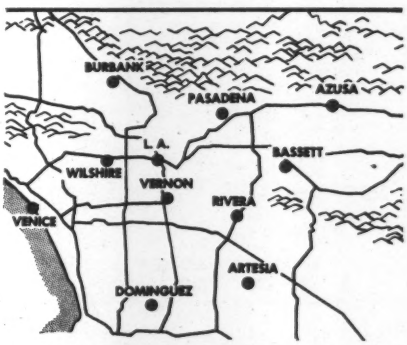

Fig. 1. Location of sampling stations in Los Angeles Basin.

Operations

Since meteorological conditions are a prominent factor in this phenomenon, the location of 10 sampling stations along typical paths of air flow was based on previous meteorological studies[3]. The location of sampling stations is shown in Fig. 1.

Continuous recording instruments were procured for some measurements. Manpower and time limitations did not permit manual sampling at all stations for other variables. The items measured and procedures used are shown in Table I.

Detailed descriptions of instruments and methods of analysis have been published[2, 1]. Actual measurements and operations were conducted by various organizations supported either by contract or by grant.

Over 150,000 measurements were made during this 4-mo. survey. Data were transferred to IBM cards to facili-

[1] Proc. Third Natl. Air Pollution Symposium. Stanford Research Inst., Los Angeles, Calif., p. 12 (Apr. 1955).

[2] W. L. Faith, L. B. Hitchcock, M. Neiburger, N. A. Renzetti and L. H. Rogers. First Tech. Progress Rept., Air Pollution Foundation, Los Angeles, Calif. (1955).

* Presented at the Minneapolis meeting of the American Chemical Society, Sept. 13, 1955.

[3] Morris Neiburger and James G. Edinger. Meteorology of the Los Angeles Basin. Air Pollution Foundation Rept. No. 1 (1954).

TABLE I

Aerometric Survey, 1954

Variable	No. of Stations	Procedure
Eye irritation	10	Panels of 12 or more people
Oxidant	11	Continuous Beckman oxidant recorder.
Plant damage	6	Pinto beans
Aldehydes	5[a]	Midget impingers; bisulfite; titration.
Carbon monoxide	5[a]	MSA color tubes.
Hydrocarbons	5[a]	Cold traps, infrared.
Inversion height	1	Radiosonde.
Wind data	58[c]	Anemometer; vanes.
Nitrogen oxides	7[a]	Rotating sampler; evacuated bottles. Rider-Mellon
Particulate matter	2	Hemeon sampler; physical and chemical analysis.
Particulate matter	2	Staplex sampler; Chemical analysis.
Solar radiation	4[d]	Pyrheliometer.
Sulfur dioxide	2[b]	Thomas autometer.
Temperature and humidity	6	Hygrothermographs.
Upper air (oxidant, oxides of nitrogen)	3	Blimp
Visibility	4	Transmissometers.

(a) 3 stations by Air Pollution Control District.
(b) 1 station by Air Pollution Control District.
(c) Data collected by Air Pollution Control District.
(d) Two Weather Bureau stations, one by Univ. of Calif. and one by Air Pollution Foundation.

tate calculations. Procedures employed in data reduction and in preparation of punched card and tabular records have been described[4].

Of the 16 items shown in Table I, several were measured because they were thought to be either attributable to smog effects or derivatives of primary smog-forming components.

Correlations between Variables

The statistical studies were carried out by E. J. Wiggins[5]. The principle function of the statistical procedure employed in this study was to obtain correlations between pairs of variables at particular locations or times. The basic method of expression of this information is a regression equation relating corresponding pairs of values of the 2 variables. The coefficients of the equation show the form of the relationship between the 2 variables, while the dispersion about the regression line indicates how much of the variance of the dependent variable is due to the assumed form of the relationship and how much to additional variables and experimental error.

The general form of regression equation adopted for the analysis is the quadratic $y = A + Bx + Cx^2$. This expression provides for threshold values of either variable, for positive or negative slopes, and for upward or downward curvature. It therefore allows most of the probable forms of relationships between variables to be approximated, although it is possible that specific cases might be encountered where this equation does not provide the best approximation.

The coefficients of the regression equation are calculated to minimize the deviation of experimental points around the regression line, and therefore to provide the best fit possible with this particular form of equation. The mere existence of a good fit does not indicate a definite relationship between the 2 variables, since the regression line might be nearly horizontal or vertical. Also the shape of the regression curve, which provides the best fit may not be significant if the dispersion is large, since a quite different curve might give only a slightly lower index of correlation. It is therefore

[4] N. A. Renzetti (ed.) An Aerometric Survey of the Los Angeles Basin, Aug.-Nov. 1954, Air Pollution Foundation, Los Angeles, Calif. p. 89 (1955).

[5] Ibid., p. 226.

TABLE II

Eye Irritation Values[a]

Station	Total Days of Sampling	% of Days Mean Severity above 25	Highest Value
1. Venice	22	5	25
2. Wilshire	33	42	40
3. Downtown	48	27	38
4. Pasadena	28	46	44
5. Burbank	28	58	39
6. Dominguez	21	10	25
7. Artesia	23	9	25
8. Rivera	33	35	38
9. Bassett	28	35	35
10. Azusa	27	44	38

(a) The scale of units for eye irritation is abitrarily established where 5 is threshold, 25 moderate, and 35 or higher is severe. It is based on statistical evaluation of systematic, subjective observations by panels of 20 to 30 regular observers located at each of the 10 stations. The scale runs from 0 to 55 units.

TABLE III

Significance of Correlations Between Eye Irritation and Instantaneous Values of Other Variables

Eye Irritation	Oxidant	NO_2	SO_2	CO	HC	Visby	Temp.	RH	Part.	Ald.	COH
Stn. 1	N	N									
2	N	N		S	S	N	N	N		N	
3	S	N	X	S	S		N	N	S	N	S
4E	S	N			S	S	N	N	S	S	S
4L	S	N		S	S	S	N	X	X	S	S
5	S	N									
6	N	N		N	N	N	N	N		N	
7	N										
8	S						N	N			
9	S						N	X			
10	S										
All	S	S		S	S	S	N	N	S	S	S

The symbol S indicates significance at the 5% level,
X indicates significance at the 5% to 30% level, and
N indicates significance poorer than 30%.
E indicates expert panel
L indicates lay panel

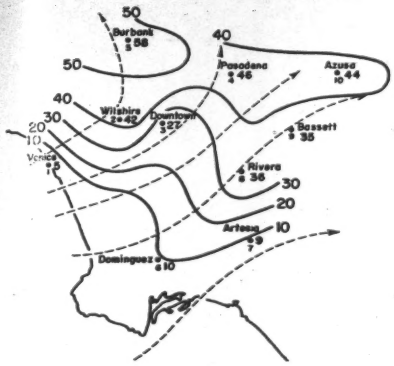

Fig. 2. Percentage of sampling days with eye irritation greater than 25 on scale 0-55.

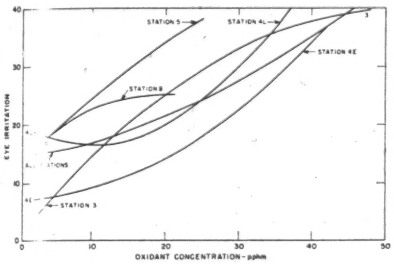

Fig. 3. Regression curves relating eye irritation and oxidant concentration.

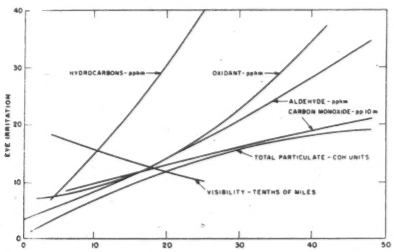

Fig. 4. Regression curves relating eye irritation and other variables at Station 4—expert panel.

necessary to consider both the coefficient of the equation and the index of correlation in deciding whether a significant relationship exists between 2 variables. A significant correlation can be taken as an indication of association between 2 variables, but it is important to realize that this does not automatically imply causation.

Eye Irritation

Eye irritation panels of 12 or more individuals were used. A graphic form was filled out by each individual on the days when observations were made to indicate a subjective estimate of the intensity of eye irritation on a scale of 0 - 55. A more complete description of the method and its limitations have been given by P. R. Merrifield[6].

As one example of the results, observations were summarized by calculating

[6] Ibid., p. 36.

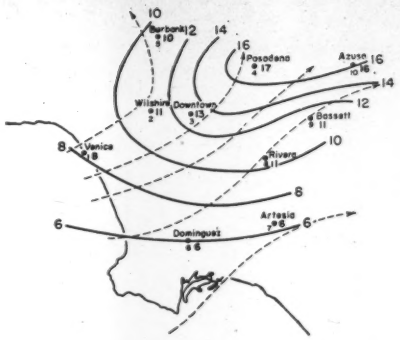

Fig. 5. Average daily maximum oxidant concentration (pphm.) Aug.-Nov. 1954.

the per cent of the days sampled at each station when mean the severity was above the value of 25. These data appear in Table II.

When plotted on a map, a systematic pattern emerges. This is shown in Fig. 2. The lines of constant mean (or mean maximum) eye irritation are the solid lines; dotted lines represent the typical air streams. Thus, if one follows the air stream from Venice through the Wilshire station to Burbank, mean eye irritation values are seen to rise progressively. If one follows the air stream through Station 6 at Dominguez through Rivera and Bassett, one encounters similarly increasing eye irritation. These results are therefore consistent with the hypothesis that the pollutants and reaction products, among which is the eye irritant, increase in concentration with distance traveled over source areas.

Eye Irritation and Other Variables

The correlations between eye irritation measurements and simultaneous values of other variables are summarized in Table III. Hourly particulate concentration (in COH units)* shows significant correlations with eye irritation at the 2 stations at which it was measured. Following in descending order of numbers of stations at which significant correlations were observed are oxidant, total hydrocarbons, daily average particulate concentration, visibility, carbon monoxide, and aldehydes. Temperature, relative humidity, NO_2, and SO_2 do not yield significant correlations with eye irritation for any station.

Eye irritation observations by the *expert panel* at Station 4 yield significant correlations with more other variables than at any other station. Station 3 and the *lay panel* at Station 4 exhibited somewhat fewer significant correlations than the *expert panel* at Station 4. Station 2 had still fewer significant correlations, and Station 6 had none. Stations 1, 5, 7, 8, 9, and 10 are not comparable on this basis because of the smaller number of variables measured. When the values from all stations are combined, significant correlations are obtained with all variables except temperature and relative humidity. In the case of NO_2, the composite correlation is significant even though none of the individual stations yield significant correlations.

* Defined as that quantity of light-scattering solids producing an optical density of 0.01 when measured by light transmission through a filter.

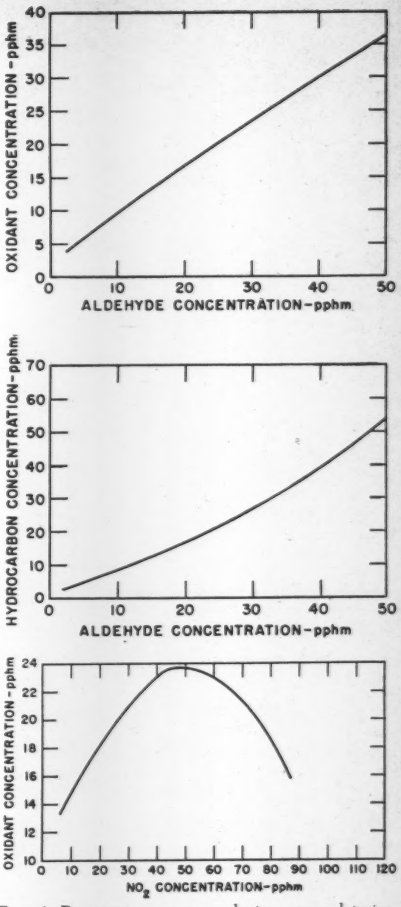
OXIDANT CONCENTRATION - pphm
ALDEHYDE CONCENTRATION - pphm
HYDROCARBON CONCENTRATION - pphm
ALDEHYDE CONCENTRATION - pphm
OXIDANT CONCENTRATION - pphm
NO2 CONCENTRATION - pphm

Fig. 6. Regression curves relating several pairs of variables.

Typical regression curves relating eye irritation and oxidant concentration for the various stations are shown in Fig. 3 and the curves relating eye irritation with the other variables for one particular station (expert panel of Station 4) are shown in Fig. 4.

The severity of eye irritation increased as oxidant increased and the relationship was approximately linear for oxidant concentration above 10 pphm.

The positive intercept on the Y-axis, implying the existence of eye irritation with zero values of contaminant, can probably be explained by 2 factors: the

TABLE IV

Average Maximum Oxidant Concentration at Eleven Stations, August - November 1954

Station No.	Location	Average Maximum Concentration (pphm.)				
		Aug.	Sept.	Oct.	Nov.	All 4 Mo.
1	Venice	6	7	9	13	8
2	Wilshire	8	8	15	14	11
3	Downtown	13	15	16	11	13
4	Pasadena	13	18	21	15	17
5	Burbank	11	11	15	10	10
6	Dominguez	6	6	7	7	6
7	Artesia	7	8	6	7	6
8	Rivera	11	11	12	11	11
9	Bassett	13	8	15	9	11
10	Azusa	18	16	21	13	16
12	Santa Barbara	5	7	8	7	6

tendency of some observers always to report eye irritation for psychological reasons which cannot be offset by any *negative* values; and the arrangement of the form used for reporting eye irritation in the survey, in which the *none* heading was a finite distance along the scale.

The positive slopes of all curves relating eye irritation with contaminant concentration might seem to suggest that eye irritation results from these contaminants. However, since meteorological conditions are a common factor in all of these measurements, and since some of the suspected major sources produce several of these contaminants simultaneously, the concentrations of all contaminants tend to rise and fall together. The observed eye irritation might therefore be produced by only one of the measured contaminants or by some unknown material which is present in concentrations proportional to those of the other materials.

The family of curves relating eye irritation with other variables at Station 4 shows that eye irritation increases with increasing concentration of hydrocarbons, oxidant, aldehydes, carbon monoxide, and total particulate, and decreases with increasing visibility. The latter result appears to follow directly from the fact that visibility decreases with increasing concentrations of aerosol material. At the time of day when eye irritation observations were made, this aerosol material would be almost entirely derived from human activity rather than natural fog and would be a quantitative index of air pollution.

The slopes of the curves relating eye irritation with the concentrations of various contaminants differ considerably, as shown in Fig. 4. However, the slopes of the curves cannot be used to infer the relative sensitivity of the eye to these materials, since the ratio of the slopes merely reflects the ratio of the concentrations at the time of the measurements.

In the cases mentioned, where significant correlations are obtained between eye irritation and contaminant concentrations, it is inferred that eye irritation may actually be the result of the presence of one or more of these contaminants. In the remaining cases, where the correlations are not statistically significant, several interpretations are possible; there may be no relationship whatever between eye irritation and the other variables; there may be independent variables which produce a large variance in one or both of the correlated variables; or the various sources of error in the measurements may result in a dispersion which is too large to yield a significant correlation with the available number of measurements. In the case of a set of correlations which are statistically significant as a group but not for individual stations, such as eye irritation and NO_2, it is reasonable to infer that the last explanation may be correct. In the case of a station which yields no significant correlations between eye irritation and any other variable, such as Station 2, it may be reasonable to infer that independent variables, such as meteorological conditions, are involved.

Oxidant

Oxidant was measured at 10 stations in the Basin and at Santa Barbara with a continuous recording colorimeter using neutral buffered potassium iodide solution as the reactant.

Oxidant began to increase all over the basin at about the same time of day, suggesting that the material from which oxidant was formed was *widely* distributed. Since the peak of oxidant formation shifted approximately one hr. when human activity shifted from daylight to standard time, it is indicated that the pollutants which gave rise to oxidant formation originate from human activity. The highest oxidant values on any one day may occur anywhere in the basin, although preferentially in the north and east.

The attacks occurred during daylight hours, peaking during the middle of the day.

To summarize the oxidant data from the 11 stations, Table IV was compiled.

Table IV indicates that Santa Barbara, Artesia, and Dominguez stations, closely followed by the Venice station, exhibited the lowest average oxidant values, all 4 having concentrations in the range of 6 pphm. to 8 pphm. The Burbank, Rivera, Bassett, and Wilshire stations had average concentrations varying from 10 pphm. to 11 pphm.; and the downtown Azusa, and Pasadena stations showed average concentrations from 13 pphm. to 17 pphm. Thus, there was a general trend for lower oxidant concentrations to occur at the stations windward of the Los Angeles central business district and higher values down-wind.

This trend is shown more clearly in Fig. 5., the average values from Table IV are plotted for each station, and lines of equal average peak oxidant values are drawn. While these lines must be regarded as tentative, since the data for four months are not adequate to establish a *normal* pattern, their regularity suggests the plausibility of the following hypothesis.

In accord with the laboratory results of Haagen-Smit, it is postulated that the oxidant concentration depends on the concentration of reactants, presumably

TABLE VI

Summary of Survey Station Records, August to November, 1954 for Number of Days Data Collected, Days with Plant Damage, Range of Injury Indexes, Mean Plant Injury Indexes, and Oxidant Values.

Station	Number of days		% days	Plant injury indexes[a]		Oxidant pphm.	
	Recorded	Plants Damaged	Plants Damaged	Range	Mean	24-hr. mean	Max.
Los Angeles (3)	74	65	87.8	0-3.6	0.72	5.96	16.1
Pasadena (4)	74	59	79.7	0-3.6	0.68	6.71	19.7
Dominguez (6)	74	61	82.4	0-4.5	0.70	3.47	9.3
Rivera (8)	74	63	85.1	0-6.3	0.77	5.47	13.0
Bassett (9)	67	56	83.6	0-6.3	0.74	4.42	12.1

(a) Based on a range of 0 to 10 where 0 is no damage, and 10 reflects 100% damage to leaf tissue.

hydrocarbons and NO_2, and the intensity of radiation. The solar radiation reaches its peak value near noon, and the concentration of reactants depends on the time spent over pollution sources and the number and strength of the sources.

The sea breeze carries air inland from the ocean, so that at stations near the coast polluted air has been replaced by air which has spent only a short time over land before the solar radiation had reached its maximum, but the air at inland stations at that time, when photochemical reaction rates would be greatest, has passed over large areas of industrial, residential, and traffic sources. The increase of peak oxidant values with distance inland is thus consistent with the theory that oxidant is a product of photochemical reaction involving contaminants introduced into the air as it moves across the basin.

Oxidant and Other Variables

The correlations between the values of various pairs of variables at the time of maximum oxidant concentration are summarized in Table V.

The regression curves for several pairs of variables at station 4 are plotted in Fig. 6. The curve relating hydrocarbon and aldehyde concentrations indicates approximately a 1:1 ratio between these materials.

The good correlations between aldehyde and oxidant concentrations at stations 3 and 4, in spite of the lack of significant correlations between carbon monoxide or hydrocarbons and oxidant concentrations at these stations, suggest there may be some real connection between these two variables. Such an inference would be in line with the various postulated mechanisms of formation of oxidant and aldehyde by photochemical reactions.

The curve relating oxidant and nitrogen oxide concentrations rises to a peak at approximately 50 pphm. and then falls off again rapidly. The shape of this curve is quite similar to those obtained by Haagen-Smit[7] in laboratory experiments, and the position of the maximum (0.5 ppm. NO_2) is close to that which would be obtained by extrapolation of Haagen-Smit's curves to hydrocarbon concentrations of the order of 0.2 ppm.

Plant Damage

The Pinto bean was selected from a number of plant species because of its susceptibility to several air-borne phytotoxicants. A plant test chamber 2 ft. x 3 ft. x 4 ft. in size, was constructed of plywood. A transparent plastic covering was provided so that sufficient light was transmitted into the box for the plants. A small squirrel-cage fan was provided to circulate air through the box. Five pots of plants were placed in each box each day and transported to and from an activated-carbon-protected greenhouse in a similarly protected truck. Other details have been published by Middleton et al.[8]

Data were collected for plant damage over a 121-day period at six stations by Middleton and co-workers[8], and the following discussion and interpretation is largely theirs.

Data for station 2, Wilshire, are omitted since the relative humidity and

TABLE V

Significance of Correlations Between Variables at Time of Maximum Oxidant

Plant Damage	Oxidant	NO_2	SO_2	CO	HC	Vis'y	Ald.	Temp.	RH	COH	Pb
St'n. 2	N	N	N	N	N	N	N	N	N		
3	S	N	N	N	N		N	N	S	S	N
4	S	N		N	S	S	S	N	S	N	N
6	N	N			N	S	N	N	X		
8	N							N	S		
9	N							N	N		
All	S				X	N	S	N	S	S	
Oxidant											
St'n. 1		N									
2		N	N	N	S		S	N	S		
3		N	S	N	N		S	N	S	S	S
4		S		N	N		S	N	S	S	S
5		S									
6		N					X	N	S		
8								N	X		
9								S	N		
All		N					S	N	S	S	S
Visibility											
St'n. 2	N	S	N	S	S		S	N	N		
4	N	N		N	N		N	N	N	S	S
6	N	X			N			N	N		
All											
NO_2											
St'n. 2			N	N	N		N	N	N		
3			N	N	N		N	N	N	S	S
4				S	S		S	N	N		N
6				N	S		N	N	N		
All				N	N		S				
SO_2											
St'n. 2				N	N		N	N	N		
3				S	N		N	N	N	S	N
All											
CO											
St'n. 2					S		S	N	N		
3					S		S	N	N	S	S
4					S		S	N	N	S	N
6					S		N				
All					S		S			S	
HC											
St'n. 2							S	N	N		
3							S	N	N	S	S
4							S	N	S	S	S
6							N	N	S		
All							N				
Ald.											
St'n. 2								N	N		
3								N	S	S	S
4								N	N	S	S
6								N	N		
All										S	

The symbol S indicates significance at the 5% level, X indicates significance at the 5% to 30% level, and N indicates significance poorer than 30%.

[7] A. J. Haagen-Smit and M. M. Fox. *Air Repair* 4, 105 (Nov. 1954).

[8] Proc. Third Natl. Air Pollution Symposium. Stanford Research Inst., Los Angeles, Calif., p. 191 (Apr. 1955).

TABLE VII

Summary of Station Mean Plant Injury Indexes of Oxidant 24-hr. Mean Class Ranges for all Days of Complete Record, 1954.

Station	Mean plant injury indexes					
	Oxidant 24-hr. mean class range pphm.					
	0-2.5	2.6-5.0	5.1-7.5	7.6-10.0	10.1-12.5	12.6-15.0
Los Angeles (3)	0.15	0.62	0.61	1.28	1.30	
Pasadena (4)	0.15	0.30	0.67	0.96	0.98	0.80
Dominguez (6)	0.75	0.54	1.30	1.05		
Rivera (8)	0.53	0.81	0.75	0.79		
Bassett (9)	0.70	0.72	0.62	4.30		

temperature records as well as plant responses indicated an indoor atmosphere rather than an outdoor one. All the data collected were reviewed and it was determined that there were 74 days of adequate record for Los Angeles, Pasadena, Dominguez, and Rivera, and 67 for Bassett. This reduction in number of days from the total length of the survey was occasioned by missing plants, unsuitable replication, unsuitable biological material due to short hypocotyl length and small leaf size, occasional failures in the plant production glasshouse, and missing oxidant mean and oxidant maximum records. A summary of the days of record, the per cent days upon which plants were damaged, and the plant injury index ranges are given in Table VI.

Plants were damaged 79.7% of the time at Pasadena, and 87.8% of the time at Los Angeles, with intermediate values for Dominguez, Rivera, and Bassett.

The damage regularly observed was similar to that produced by oxidized hydrocarbons. The test plants did not show ozone damage, even though the oxidant values were high enough to have produced typical ozone damage, distinct from smog damage, if the oxidant is mainly ozone.

The plant injury index ranges varied from 0 to 3.6 for both Los Angeles and Pasadena, from 0 to 4.5 for Dominguez, and from 0 to 6.3 for both Rivera and Bassett. The mean injury indexes ranged from a low of 0.68 for Pasadena to a high of 0.77 for Rivera, with intermediate values for the remaining stations. There is no statistically significant difference between any of the mean plant injury indexes.

The mean plant injury indexes for selected class ranges of oxidant 24-hr. mean values are presented in Table VII. An analysis of these data is presented in Table VIII which shows that there is a significant correlation of injury index with oxidant 24-hr. mean for both Los Angeles and Pasadena, but not for Dominguez, Rivera, and Bassett. When the combined station values are analyzed, there is no statistically significant correlation between the plant injury indexes and the oxidant 24-hr. mean values.

Conclusions

Smog as manifested by high average oxidant concentration occurred throughout the Los Angeles Basin. Attacks were consistently most severe in Pasadena, Azusa, and downtown Los Angeles; next in severity were the Wilshire district, Burbank, Rivera, and Bassett; and least were Venice, Dominguez, and Artesia.

Smog as manifested by human eye irritation occurred throughout the Los Angeles Basin, with the maxima in Burbank and Pasadena. Severity of eye irritation increased as oxidant increased for values of the latter above 10 pphm.

The measurement of oxidant concentration constitutes the best available objective indicator of the severity of smog.

Lines of equal oxidant and eye irritation values resemble contour lines on a topographic map. Typical air streams crossing these contours from the ocean to the foothills go from low to high values, apparently corresponding to the length of time the air has spent over source areas, the number and strength of pollutant sources encountered on the way, and the amount of insolation the air has experienced. These indicators are broadly consistent with the laboratory findings of earlier investigators of photochemical oxidative reactions.

Smog as manifested by damage to plants occurred throughout the basin. It occurred in 80 to 88% of the days of this survey when normal experimental conditions existed. The correlation between the injury index, or quantitative estimate of damage, and oxidant is below the level of significance. However the per cent of plants damaged, or the qualitative estimate of injury, is significantly correlated with oxidant.

The correlations among oxidant, aldehydes, hydrocarbons, and oxides of nitrogen are broadly consistent with the postulate proposed previously on the basis of laboratory experiments by Haagen-Smit and others which have demonstated that oxidants and aldehydes are produced by photochemical reactions between hydrocarbons and oxides of nitrogen under the influence of sunlight.

Acknowledgment

The authors are indebted to the Los Angeles County Air Pollution Control District, for advice, and support, in addition to experimental data. Thanks are also due to P. R. Merrifield, J. T. Middleton, and E. J. Wiggins for conducting phases of the aerometric survey and analyzing obtained data.

TABLE VIII

Coefficients of Correlation for Plant Injury Indexes and Oxidant 24-hr. Means for all Days of Complete Record, 1954.

Station	Coefficients of correlation		
	Injury index and oxidant	Values required for significance at	
		19:1	99:1
Los Angeles (3)	0.95	0.88	0.96
Pasadena (4)	0.85	0.81	0.92
Dominguez (6)	0.64	0.95	0.99
Rivera (8)	0.71	0.95	0.99
Bassett (9)	0.62	0.95	0.99
Combined	0.75	0.81	0.92

Meteorology as Related to Reactor-Site Selection

(Continued from page 153)

determine if wind shifts are likely or if precipitation may occur and cause a large fraction of the cloud material to deposit on the ground thus greatly increasing local dosage and prolonging the effects of the incident.

To conclude, it is evident proper meteorological assistance and guidance can be of value to site selection, engineering design, and actual operation of atomic energy plants.

The Formation of Ozone in the Los Angeles Atmosphere*

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Stanford Research Institute
Pasadena, California

In working with complex reactions such as those occurring in Los Angeles smog 2 approaches can be used. Either a simplified system containing only a few components of known concentrations is used, or outside air is used as a substrate for experimentation.

While the former approach is better suited for elucidation of reaction mechanisms it is impractical to attempt mechanism studies with a complex urban atmosphere—the use of simplified systems is characterized by the danger that the reactions studied may not go at all, or may lead to different products when carried out in the presence of the multitude of compounds normally present in the urban atmosphere. The best approach requires use of both techniques. The work with outside air establishes the framework within which model reactions have to perform; it is only by frequent reference to the framework that we can avoid operating in a *vacuum*.

Work described in this paper represents primarily the first step in an attempt to characterize reactions leading to formation of oxidant in Los Angeles. The composition of oxidants occurring in the Los Angeles atmosphere is complex. Considerable evidence indicates that the bulk of this material consists of ozone[3].

[3] F. E. Littman and C. W. Marynowski. Identification of Ozone in the Los Angeles Atmosphere. **28** 819, (1956).

* Presented at the 128th National ACS Meeting, Minneapolis, Minn., Sept. 11-16, 1955.

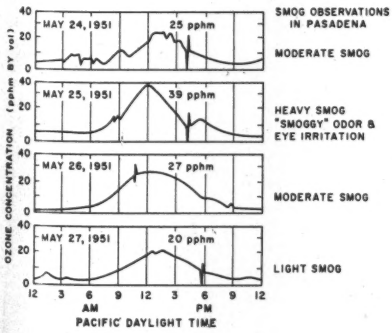

Fig. 2. Typical Ozone Concentration Records.

The characteristic diurnal changes in concentration, paralleling the amount of available sunlight, suggested that oxidant was produced by the action of light. This assumption was furthered when it was demonstrated an oxidant could be formed by irradiation of night air with artificial light.

Other possible sources of ozone had been examined, but neither electrical discharges nor transportation from the upper atmosphere could be substantiated experimentally. Photochemical formation seemed unlikely because wavelengths necessary for the dissociation of oxygen are not available at sea level. The indirect formation of ozone with a substance other than oxygen acting as light absorber, was considered. Recent experimental evidence lends this hypothesis credence.

Fig. 1. Continuous Oxidant Recorder.

The daily fluctuations of oxidant concentration have been followed for years at the Institute's Pasadena Laboratory by means of an automatic oxidant recorder (Fig. 1)[4]. Typical oxidant curves (Fig. 2) show a characteristic pattern with low concentrations of oxidant at night, increasing to a maximum around noon, and disappearing again at sunset. Maximum concentrations vary with values as high as 60 pphm. occuring during smoggy weather. Concentrations at night seldom exceed 5 pphm. Variations from day to day are greater than those from month to month. An annual cycle exists, with high concentrations occuring more frequently from May through October than during the rest of the year.

If air is irradiated with *artificial sunlight* before entering the recorder, a different pattern results. The experimental arrangement used is shown in Fig. 3. Air was passed through a 50-*l.* flask irradiated with 4 H400 E-1 mercury vapor lights. The average residence time of the air was about 20 min. The mercury arcs gave off no radiation below about 3000 Angstroms, and were incapable of forming ozone directly by oxygen dissociation. A typical oxidant pattern resulting from this arrangement is shown

[4] F. E. Littman and R. W. Benoliel. Continuous Oxidant Recorder. *Anal. Chem.* **25**, 1480 (1953).

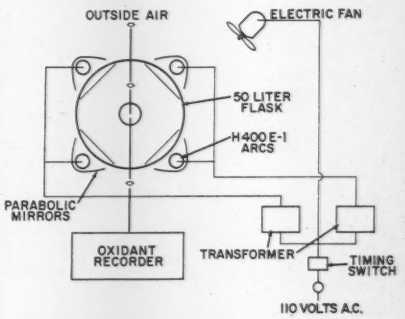

Fig. 3. Diagram of single-flask precursor recording system.

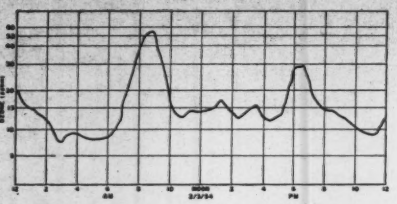

Fig. 4. Daily variations of ozone formed by constant irradiation of outside air.

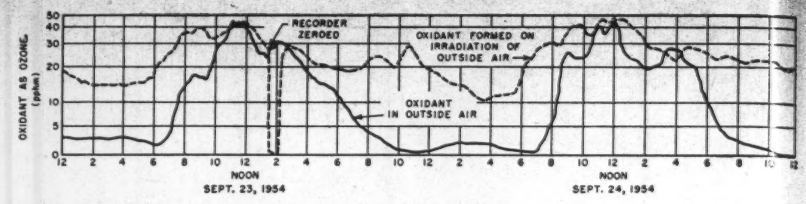

Fig. 5. Oxidant formed by constant irradiation of outside air—Sept. 23-24, 1954. Precursor trace includes oxidant present in air.

in Fig. 4: the characteristic division between daytime and nighttime has disappeared, and oxidant concentrations of the same magnitude as those existing in the daytime resulted from irradiation of night air.

Continued monitoring of outside air showed that the oxidant formed by irradiation of night air followed a daily and annual cycle. The daily cycle frequently showed 2 maxima, one around 7:00 P.M., the other about 8:00 A.M. High oxidant concentrations could be formed regularly by irradiation of night air during fall and winter, from September through March. During the summer months little, if any, oxidant was formed at night, despite the fact that high concentrations occurred in the daytime during that period.

The observation that oxidant could be formed experimentally by action of light on polluted urban air led to an investigation of those impurities in air which, upon irradiation, formed oxidant. The term *oxidant precursors* was coined to describe these materials, and a series of experiments was started to determine their physical and chemical properties.

That light was responsible for formation of oxidant was demonstrated by using 2 oxidant recorders, one indicating oxidant concentration in untreated air, the other in irradiated air (Fig. 5).

Attempts were made to determine the region of active light by use of optical cut-off filters. The results, summarized in Table I, indicate that the primary light acceptor(s) absorb in a rather broad region beginning near the short wave end of the visible spectrum and extending to below 3600 Angstroms.

Fig. 6 shows the output of mercury vapor lamps and regions of transmission for various filters.

Attempts were made to determine some chemical properties of the precursors by subjecting air (prior to irradiation) to action of various scrubbers, in an effort to remove precursors. These experiments indicated that passage through a bed of activated carbon or through a combustion furnace at 760°C. removed or destroyed precursors. When incoming air was scrubbed counter-currently through packed columns 4 ft. long using 5% sodium hydroxide, the bulk of oxidant precursors remained (Fig. 7), although the concentration of such acid gases as carbon dioxide, sulfur dioxide and nitrogen dioxide was greatly reduced by this procedure. Similarly, a 5% solution of semicarbazide buffered to a pH of 4 with phosphoric acid had no effect (Fig. 8), although this agent effectively removes carbonyl compounds such as aldehydes and ketones. A particle filter, capable of removing particulate material down to 0.2 μ diam., had no effect (Fig. 9).

Freeze-out traps were used to separate or trap precursors. A trap packed with stainless steel helices and cooled in dry ice-acetone produced no significant reduction in the amount of oxidant formed upon irradiation of air passed through the trap (Fig. 10). When a liquid oxy-

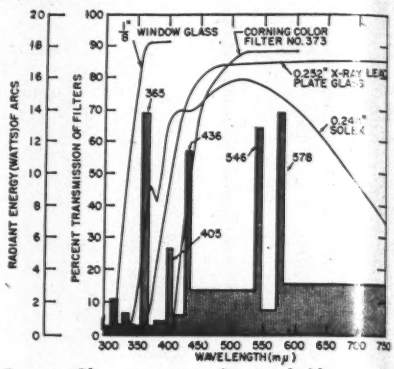

Fig. 6. Characteristics of optical filters and output of H400 E-1 arcs.

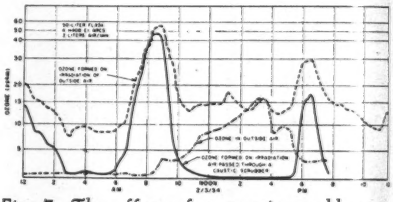

Fig. 7. The effect of a caustic scrubber on ozone formation.

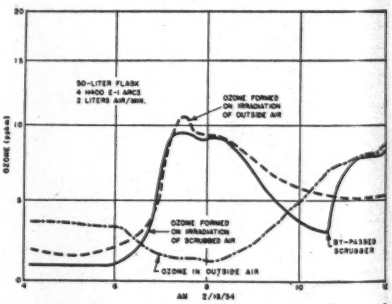
50-LITER FLASK
4 HANOVIA E-1 ARCS
2 LITERS AIR/MIN.
OZONE FORMED ON IRRADIATION OF OUTSIDE AIR
OZONE FORMED ON IRRADIATION OF SCRUBBED AIR
BY-PASSED SCRUBBER
OZONE IN OUTSIDE AIR

Fig. 8. The effect of semicarbazide and caustic scrubbers on ozone formation.

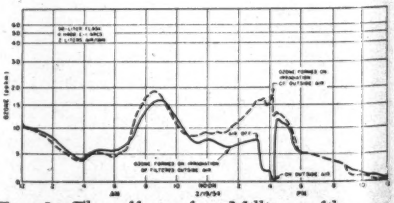

Fig. 9. The effect of a Millipore filter on ozone formation.

TABLE I

Effect of Cut-Off Filters on Oxidant Formation

Filter	Cut Off Below	Results
Light envelope and flask walls	2800 Angstroms	Maximum ozone formation
1/8 in. window glass	3100 Angstroms	No reduction of ozone level
Solex glass	3400 Angstroms 50% reduction at 3650 Angstroms	Definite, small reduction in ozone
X-ray lead glass	3700 Angstroms	Ozone level reduced 50%
Corning glass filter No. 373	4000 Angstroms	Substantially complete reduction of ozone formation

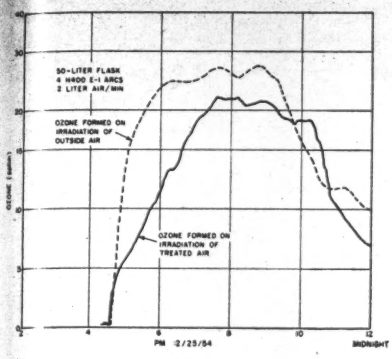

Fig. 10. The effect of dry ice cold trap on ozone formation.

gen-cooled trap was used in series with the dry ice trap, essentially complete retention of the oxidant precursors resulted (Fig. 11). Upon removal of the coolant bath, the bulk of the precursors was released, as the same figure indicates.

This technique for collection and concentration of substances yielding oxidant on irradiation promised to make their analysis feasible and gave hope for eventual identification.

Numerous freeze-out collections were made and analyzed. The train used is shown schematically in Fig. 12. Air was drawn through a semicarbazide column and a caustic scrubbing column. The stream was then split: one half passed through an irradiated flask and then into a series of traps; the other half passed through a dark flask on its way to the traps. By examining contents of the traps we hoped to obtain a differential analysis since irradiation should introduce a change which could be picked out from the general background common to the dark and irradiated samples.

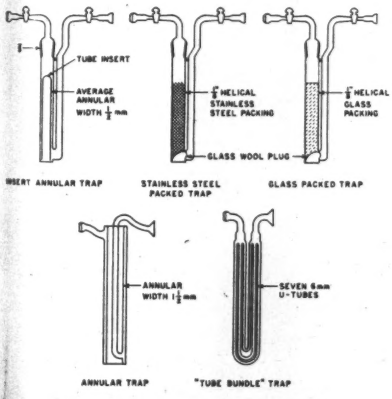

Fig. 13. Freeze-out trap designs.

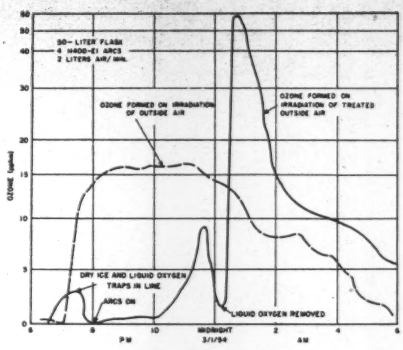

Fig. 11. Liquid oxygen cold trap as a method for collecting and storing precursors.

Various trap designs were tried; a few are shown in Fig. 13. Over-all efficiency for both retention and desorption is compared in Table II. From this tabulation it appears that traps packed with stainless steel helices gave best precursor recovery.

The samples were analyzed using infrared, ultraviolet, and mass spectrometric methods. After collection in liquid oxygen-cooled traps, samples were kept in liquid nitrogen. After connections were made to the mass spectrometer, the noncondensable fraction was pumped off and the remaining sample was introduced into the inlet system by gradually warming the trap to room temperature. Samples for infrared and ultraviolet analyses were handled similarly but transfer was accomplished by freezing the sample over into an optical cell equipped with a cold finger.

Results of these analyses indicated that the bulk of material retained in liquid

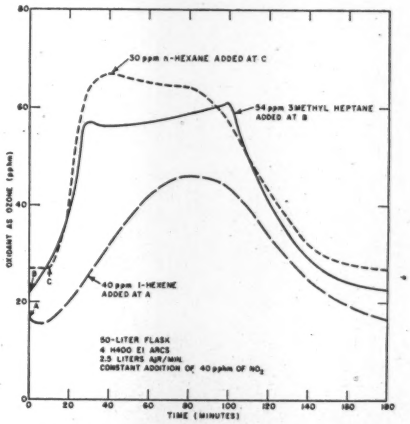
30 ppm n-HEXANE ADDED AT C
54 ppm 3METHYL HEPTANE ADDED AT B
40 ppm 1-HEXENE ADDED AT A
50-LITER FLASK
4 H400 EI ARCS
2.5 LITERS AIR/MIN.
CONSTANT ADDITION OF 40 pphm OF NO2
OXIDANT AS OZONE (pphm)
TIME (MINUTES)

Fig. 14. Oxidant formation in irradiated mixtures of various hydrocarbons with NO_2 in filtered air.

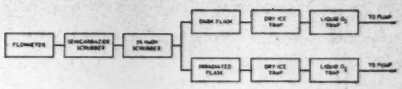

Fig. 12. Schematic diagram of sampling train.

oxygen traps consisted of carbon dioxide and water. The balance of the sample was composed of organics. The general distribution of mass peaks resembled a gasoline mass spectrum, with the high molecular end attenuated. Comparison of spectra of irradiated and nonirradiated samples showed a consistant decrease of olefin and diolefin mass peaks on irradiation (particularly m/e 39, 43 and 67), but in general there were large differences in sample composition making meaningful comparison difficult.

The infrared analyses showed absorption bands in the region of 3.4, 6.9, and 7.3 μ, which are due to carbon-hydrogen bonds: bands of 5.8 and 8.2 μ, indicative of acetone: the carbon dioxide bands of 4.3, 13.9, and 15 μ: and a doublet at 6.3, which might be due to organic nitrates. Several minor unidentified bands were present. The ultraviolet spectra showed no significant absorption bands.

Chemical analyses were performed on several samples to detect oxides of nitrogen not found by spectral analyses. A modified Griess reagent was used, and contents of several freeze-out traps were examined by venting them through an irradiated flask into a scrubber containing the reagent. Alternatively, ozone was added to the flask and permitted to react

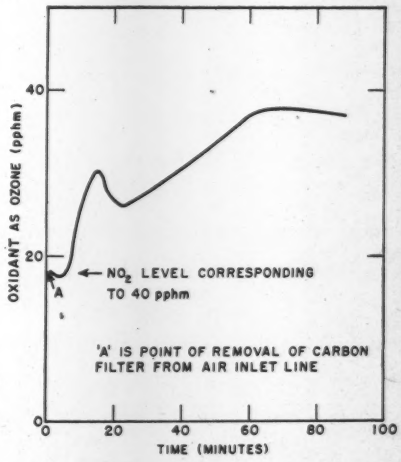
OXIDANT AS OZONE (pphm)
NO2 LEVEL CORRESPONDING TO 40 pphm
'A' IS POINT OF REMOVAL OF CARBON FILTER FROM AIR INLET LINE
TIME (MINUTES)

Fig. 15. Formation of oxidant on irradiation of nitrogen dioxide in unfilled outside air.

with its contents, since Griess reagent responds to nitrogen dioxide but not to nitric oxide. Relatively large amounts of nitrogen dioxide were found in these cases, more than could be accounted for by the nitrogen dioxide present at the time of collection. Thus nitrogen dioxide appeared to be formed during collection and/or irradiation of the air sample. This pointed toward a possible mechanism of oxidant formation.

Formation of ozone from mixtures of nitrogen dioxide and hydrocarbons has been described by other investigators[1]. A series of experiments was run using oxidant recorders and irradiated flasks. A mixture of carbon-filtered air and 40 pphm. of nitrogen dioxide was run into the recorder until an equilibrium level was established. A small quantity of a hydrocarbon was added to the flask from a syringe and permitted to flush into the recorder. The resulting oxidant curves are shown in Fig. 14. They indicate that relatively large amounts of an oxidant can be formed by irradiation of synthetic mixtures of a variety of hydrocarbons and nitrogen dioxide.

Since hydrocarbons exist in outside air it seemed important to determine whether they were capable of producing similar results. When nitrogen dioxide was added to a stream of carbon-filtered night air (at a time when no precursors were present) and when the air was passed through an irradiated flask into an oxidant recorder, a level of oxidant was established, because the recorder is somewhat sensitive to nitrogen dioxide. When the carbon filter was removed, so that the mixture consisted of untreated outside air and nitrogen dioxide, the recorder climbed rapidly to a higher level, indicating that an additional amount of oxidant had been formed (Fig. 15).

Thus, substances normally present in outside air reacted during photolysis of nitrogen dioxide to produce oxidant above that due to nitrogen dioxide.

Since we had previously demonstrated (by means of caustic scrubbers) that a substantial reduction of the nitrogen dioxide present in outside air did not have a gross effect on its oxidant-forming ability, these experiments appeared to be largely of academic interest. A possible connecting link was nitric oxide, but its known rate of oxidation to nitrogen dioxide was slow and its presence in outside air not established.

This line of research received further impetus when a nitrogen dioxide and nitric oxide recorder was developed. This instrument is based on absorption of nitrogen dioxide in Saltzman reagent[6] and subsequent colorimetric determination of the amount of nitrogen dioxide. In its simplest form it responds only to nitrite in solution (which may originate from nitrogen dioxide or organic and inorganic nitrites), but a modification of the instrument determines nitric oxide as well. This can be achieved by filtering the incoming air through activated charcoal, (which passes nitric oxide but retains nitrogen dioxide and nitrites), followed by a gas-phase oxidation of nitric oxide to nitrogen dioxide using ozone. The resulting nitrogen dioxide is determined colorimetrically.

Monitoring of Pasadena atmosphere indicated that nitric oxide is normally present in the air in quantities in excess of those of nitrogen dioxide. Concentrations of nitric oxide ranged from 2 to 30 pphm.

The rate of oxidation of nitric oxide (by oxygen) in these concentrations is slow, but under the conditions of these experiments, using irradiated 50-*l.* flasks and mixtures containing 1-10 ppm. of hydrocarbons and 0.1 - 1.0 ppm. nitric oxide, a rapid oxidation to nitrogen dioxide appeared to take place, accompanied by formation of some ozone.

The low boiling point of nitric oxide (—156°C) made retention of this gas in freeze-out traps cooled with liquid oxygen unlikely, at least on the basis of its partial pressure. Nevertheless, when experiments were set up to check this point

[1] A. J. Haagen-Smith, C. E. Bradley and M. Fox. Formation of Ozone in Photochemical Oxidation of Organic Substances. *Ind. Eng. Chem.* **45**, 2086 (1953).

[6] B. E. Saltzman. Colorimetric Microdetermination of Nitrogen Dioxide. *Anal. Chem.* **26**, 1949 (1954).

TABLE II

Efficiencies of Cold Traps in Precursor Collections

Air flow rate			2.5 *l*/min.					5 *l*/min.			10 *l*/min.
Type of trap			Tube bundle	Annular insert	Pyrex helices	S. Steel helices	Annular trap	Tube bundle	S. Steel helices	Annular trap	Annular trap
			COLLECTION EFFICIENCIES, %								
Date	Time (P.M.)	Precursor level, average (pphm.)									
11/16	10-12	23	54(100)	64(118) 68(126)	—	—	74(137)	—	—	—	—
11/17	8-10	23	30(100)	34(113)	—	45(150)	36(120)	—	—	—	—
11/18	9-11	19	41(100)	—	41(100) 54(132)	53(130)	—	—	—	—	—
11/19	7-10	25	40(100)	—	—	—	—	—	35(88)	26(65)	—
11/22	7-10	23	—	—	—	—	—	32(60)	—	—	18(34)
12/2	7-10	27	53(100)	—	—	—	—	35(66)	—	—	—
Average relative collection efficiencies			100	119	116	140	129	63	88	65	34

Collection efficiencies were based on recovery of oxidant (area under curve on recorder)
( ) indicate relative collection efficiencies based on tube bundle trap at 2.5 1/min = 100%

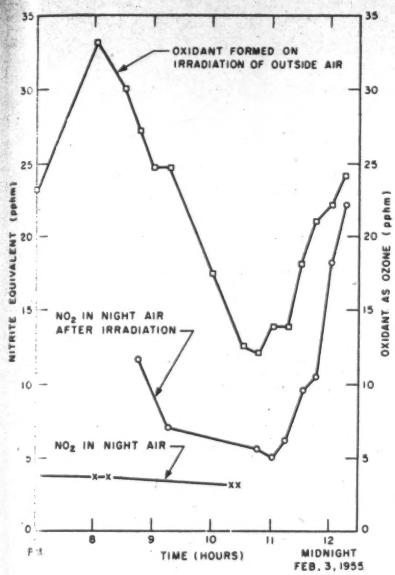
OXIDANT FORMED ON IRRADIATION OF OUTSIDE AIR
NO_2 IN NIGHT AIR AFTER IRRADIATION
NO_2 IN NIGHT AIR
NITRITE EQUIVALENT (pphm)
OXIDANT AS OZONE (pphm)
TIME (HOURS)
MIDNIGHT FEB. 3, 1955

Fig. 16. Effect of irradiation on nitrite equivalent level of night air, Feb. 3, 1955.

we found that nitric oxide was quantitatively retained. On revaporization at least part of the nitric oxide appeared in the form of nitrogen dioxide. Others, too, have observed this phenomenon[2,5].

The effect of irradiation on the oxidant and nitrogen dioxide concentrations of night air is shown in Fig. 16. Irradiation produced a significant increase of nitrogen dioxide concentration, but not enough to account for all oxidant formed.

Thus, experimental observations relating to formation of oxidant can be explained on the assumption that ozone is formed by photolysis of nitrogen dioxide, aided by a rapid conversion of nitric oxide to nitrogen dioxide in the presence of certain hydrocarbons. Quantitative aspects of such systems are under investigation.

Acknowledgments

Experimental work described in this paper was done at the Institute's Pasadena Laboratories under contract with the Smoke and Fumes Committee of the American Petroleum Institute.

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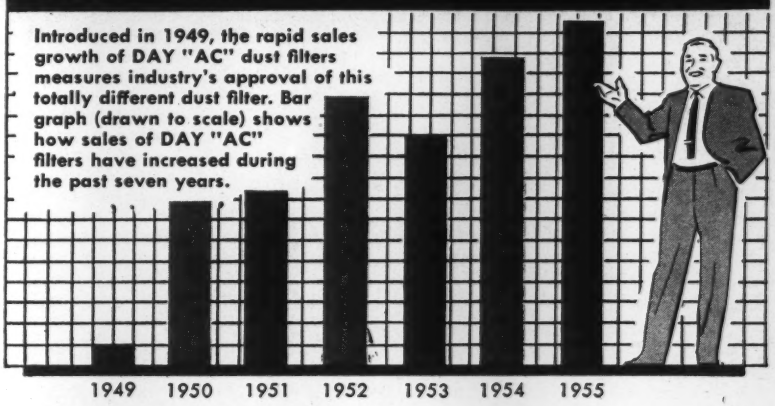
[2] F. C. Henriques, Jr., A. B. F. Duncan and Albert Noyes, Jr. Photochemical Studies—XXVII: The Effect of Radiation on Mixtures of Nitrogen Dioxide and Nitrous Oxide and Its Relationship to the Photochemical Decomposition of Nitrous Oxide. *J. Chem. Phys.* **6**, 518-22 (1938).

[5] J. Y. Macdonald. The Photochemical Decomposition of Nitrous Oxide and Nitric Oxide. *J. Chem. Soc.* (London) **1928**, 1-14.

DAY REVERSE JET DUST FILTERS

HAVE EARNED INDUSTRY'S ACCEPTANCE


Introduced in 1949, the rapid sales growth of DAY "AC" dust filters measures industry's approval of this totally different dust filter. Bar graph (drawn to scale) shows how sales of DAY "AC" filters have increased during the past seven years.
1949
1950
1951
1952
1953
1954
1955

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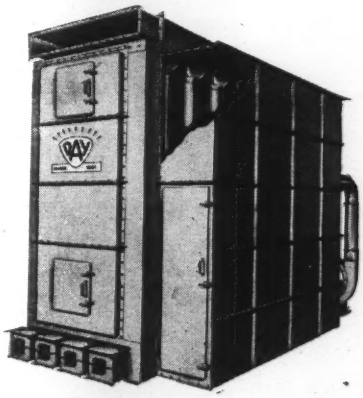

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The Joint City, County, State and Federal Study of Air Pollution in Louisville*

AUGUST T. ROSSANO, JR.
Public Health Service
Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

Louisville, Ky., like many other American cities of its size has been experiencing for some years a growing urban air pollution problem associated with its industrial and economic growth. Prior to World War II its problem was largely one of smoke and flyash, the cause of which was limited chiefly to domestic and industrial use of coal as a fuel. During the war and post-war years character of air pollution in Louisville shifted from smoke and flyash to the more heterogeneous type involving emissions of a variety of gases, fumes, dusts, and odors more characteristic of an urban complex.

The advent of World War II cut off this country's vital supply of natural rubber. To meet the growing need for rubber products, the Federal Government embarked on an intensive program of synthetic rubber production. Louisville was one of the locations selected for this purpose. In 1941 the first of a number of large plants for production of chemical rubber was built in an industrially zoned area on the southwest side of the city. Several other plants followed and within a short time there sprang up in this area a dense network of plants producing rubber or its components. The area appropriately enough became known as Rubbertown.

* Presented at the 49th Annual Meeting of the Air Pollution Control Association, Buffalo, N. Y., May 20-4, 1956.

Shortly after these plants went into production, residents of the West End, a residential area adjacent to the northern edge of Rubbertown, began complaining of discomfort from odors, dust, and eye irritation. The emergence of this new type of air pollution was generally attributed to operations in Rubbertown.

Geographic and Topographic Factors

Louisville is a city of approximately 400,000 on the south bank of the Ohio river in western Kentucky, about 100 miles downstream from Cincinnati, O. (Fig. 1) The city covers an area of 50 sq. miles on flat terrain, 400 ft. above mean sea level, representing the old flood plain of the Ohio. The adjacent terrain, across the river in Indiana to the west, rises abruptly to a range of hills running almost north and south at a maximum elevation of about 900 ft. The terrain in the other directions is flat with a few gently rolling hills.

Climatologic Factors

The climate of Louisville is the continental type affected by the westerly movement of winds and cyclonic and anticyclonic storms as well as the great source of moisture represented by the Gulf of Mexico. Winters are moderately cold with snowfall generally light. The summers are warm but rarely exceed 100°, with high relative humidity. Heavy fog, while unusual, may occur between September and March. The most frequent wind direction during th winter months is generally northerly while during the summer it is southerly Average wind speeds vary from 1 miles/hr. to about 6½ miles/hr. i August.

History of Air Pollution in Louisvil

In 1946, when urban air pollution be came significant, Louisville established Smoke Commission, which in 1951 be came the Louisville Air Pollution Con trol Commission. In July 1952, follow ing the enactment of a state air pollutio enabling act, a county-wide air pollu tion control program was establishe with creation of the Jefferson Count Air Pollution Control District, jurisdic tion of which extends to all cities withi the county.

As stated previously, almost from th initiation of operations in Rubbertown public protests of annoying dust, fumes gases, and odors began pouring in. Sev eral unsuccessful attempts were made b local citizens to bring court actio against Rubbertown industries. (Fig. 2)

Two studies were made by the Uni versity of Louisville to determine th nature and source of air pollution in th West End. In June 1952, the Battell Memorial Institute began an 18-mo study sponsored by the 8 Rubbertown industries. The findings of these studie shed some light on the problem, but be cause of their limited scope results wer

Fig. 1 & 2. Left, an artist's view of the West End of Louisville Kentucky. Above, an aerial view of the West End.

ot sufficiently conclusive to pinpoint pecific sources causing the complaints.

In July 1955, President Eisenhower igned Public Law 159, authorizing the ublic Health Service to establish a pro-ram of research and technical assistance n air pollution. Within a few days the ublic Health Service received an offi-ial request from the Jefferson County Air Pollution Control District for tech-ical assistance in dealing with the West End pollution problem. Following pre-iminary negotiations, the Service made proposal for a joint Federal, State, and ocal study. The interested agencies for-ally agreed to this proposal in October 1955, by the acceptance of a Memoran-dum of Agreement.

The purpose of this paper is to des-cribe the planning and development of his study, which was formally initiated Jan. 2, 1956. The schedule calls for 6 mo. to get the study into full scale opera-tion, 1 yr. of detailed study and observa-tion, and 3 to 6 mo. to evaluate and re-port findings.

Memorandum of Agreement

The Memorandum of Agreement is a document setting forth the terms and conditions of the study. The 4 designated cooperating agencies are the Air Pollu-tion Control District of Jefferson County, the Louisville and Jefferson County Board of Health, the Kentucky Department of Health, and the Com-munity Air Pollution Program of the Public Health Service.

The broad objectives of the study, as stated in the agreement, are to augment existing knowledge of the nature, extent, and sources of the problem as a basis for developing a rational program of con-trol. The agreement stipulates the study shall be under the technical direction of a representative of the Community Air Pollution Program of the Public Health Service, Robert A. Taft Sanitary Engi-neering Center, Cincinnati, Ohio.

A Steering Committee, consisting of 1 representative from each of the 4 par-ticipating agencies, is established to as-sist the technical director in nontechnical matters. It is further agreed the director, who also serves as executive secretary of the Steering Committee, shall present monthly progress reports to the Steering Committee. The release of nontechnical information to the general public shall be by unanimous approval of the Steer-ing Committee. Final reports are to be issued jointly by the cooperating agencies.

The budget for this study is approxi-mately $175,000 for the first year, with expectation of renewal for a second year. Federal and local contributions are approximately equal, the former being as technical services and equipment. The local contribution is largely in funds with which to procure additional per-sonnel, equipment, supplies, and services. Approximately half of the local funds were subscribed by industry.

Preliminary Operations

New personnel for the study were re-cruited through personal communication and advertisements in technical journals and local newspapers. Employment is by contract between the individual and the Jefferson County Air Pollution Control District. Responsibility for recruitment and selection as well as separation action rests with the technical director.

In addition to the technical director, the staff consists of an engineer-in-charge responsible for the operation of 4 sections, Administrative and Statisti-cal, Engineering, Chemical, and Meteor-ological Services. There are 13 full-time employees including personnel from the local Board of Health, Air Pollution Control Board, and U. S. Weather Bur-eau. In addition, there are the services of several private and governmental con-sultants. Part-time assistance is given the study by personnel from U. S. Bur-eau of Mines, National Bureau of Stan-dards, and Public Health Service.

A total of seven official agencies, in addition to the regular staff, participate in the study. Substantial financial sup-port is contributed by the industries of Louisville.

The offices for this study are in the West End and are rented on a yearly lease. The space of approximately 1,000 ft.^{2} is divided into 5 offices and 1 en-gineering laboratory. Garage space for 2 vehicles, additional engineering labor-atory operations, and storage has been leased in the vicinity. The chemical laboratories are provided by the Ken-tucky State Health Department, includ-ing 3 small laboratories, part of a larger laboratory, and use of equipment shared with state personnel.

Transportation consists of 2 automo-biles rented from the city motor pool and a panel truck and a large mobile laboratory on loan from the Sanitary Engineering Center. Instruments, sup-plies, and services other than those fur-nished by the Public Health Service are provided by the Air Pollution Control District on recommendation of the tech-nical director.

Plan of Study

To implement the broad objectives of this study, activities are being carried out along several parallel lines. The first is a determination of the quality of the air in and around the West End. This involves analyses for various particulate and gaseous pollutants, as well as a study of the variations and fluctuations in their concentrations with respect to time and space. Time considerations in-clude diurnal, seasonal, and long-range trends and patterns. The spatial factor involves comparisons of pollutant con-centrations on the basis of their horizon-tal and vertical distribution.

The second major activity is a study of the interrelationship between air quality and both meteorologic and micro-meteorologic factors.

In approaching objectives of these two phases, 4 basic principles were adopted as guides:

(1) Comprehensive or area-wide ap-proach involving a network of fixed ob-servation stations covering the area of interest.

(2) Measurements on a simultaneous and continuous basis 24 hrs./day, every day, including weekends and holidays.

(3) Sampling periods as short as practicable to obtain data suitable for estimating diurnal patterns.

(4) Through analysis of selected samples.

These principles apply to both of 2 related networks, one for air sampling and the other for meteorologic observa-tions.

In this approach, while sampling for particulates and gases is as complete as possible in terms of time and geographic area covered, intensive physical and chemical analyses are performed only on selected samples. This system permits more efficient use of limited analytic facilities since a more thorough examina-tion of significant samples is possible.

Air Sampling Network

The air sampling network (Fig. 3) is laid out on concentric arcs 2 and 3½ miles from Rubbertown as the center. Most of the stations are between 10° and 50° azimuth to provide greater cov-erage for the West End area and take into account the prevailing wind direc-tion with respect to Rubbertown as a pollution source. Stations No. 1 and 3 are the upwind and downwind stations 3½ miles from Rubbertown. Station No. 5 is on a line between Rubbertown and station No. 1 and collects data to indi-cate the influence of distance from the source. Stations No. 4 and 6 flank No. 5 and increase the chances of collecting polluted air originating from Rubber-town. These 3 stations also provide in-formation on the concentration gradient

across the polluted air stream under prevailing wind conditions. Station No. 2, also on the 3½ mile arc, is a control; that is, it collects typical samples of urban air not directly influenced by Rubbertown pollution. The use of equal distances from the source eliminates the distance factor as a variable in comparisons of station results.

In addition to those fixed air sampling stations there will in operation at least 1 mobile station built into a 1-½ ton van truck, fully equipped. This unit will sample at selected sites for limited periods of time to supplement the fixed stations.

The sampling equipment presently employed in this network is the conventional high-vol. sampler. (Fig. 4) The filter medium is glass fiber filter paper (Type 1106). Two high-vol. samplers operate alternately at each site on an 8-hr. cycle, collecting 3 samples daily/station. (Fig. 5 and 6) An automatic timer controls the change-over operation at night so that personnel need visit each station only twice daily, at 8 A.M., and 4 P.M.

Two innovations are the standard shelter, designed especially for this study, and the orientation of the main axis of the high-vol. sampler in a vertical rather than horizontal plane, minimizing any preferential effects of wind direction.

In addition, there are A.I.S.I. filter-tape samplers modified to permit analysis of particulate matter by flame photometry. Dustfall containers and adhesive surfaces are likewise provided. Collected material is subjected to special morphological examination.

The analysis of particulates collected by the high-vol. samplers consists of determinations of total loading and organic and inorganic fractions. In addition, chlorides, sulphates, and nitrates are determined by wet chemical methods. Finally, an analysis for 19 cations is made by emission spectroscopy and flame photometry (Fig. 8).

Fig. 3. Air sampling and meteorologic networks.

Nonspecific gas sampling on an intermittent basis includes the use of freeze-out traps using liquid nitrogen and evacuated glass and stainless steel flasks. Collected samples are analyzed in the mass spectrometer at the National Bureau of Standards, Washington, D. C. Specific gases are sampled by conventional means including scrubbers, absorbers, impingers, and evacuated flasks. Continuous gas sampling is presently confined to an SO_2 recorder to be supplemented later by other SO_2 units of this type as well as other automatic sampler-analyzer equipment. Under development in cooperation with the Sanitary Engineering Center are continuous gas sampling techniques utilizing plastic bags, compression cylinders, resin and activated carbon adsorption and gas chromatography.

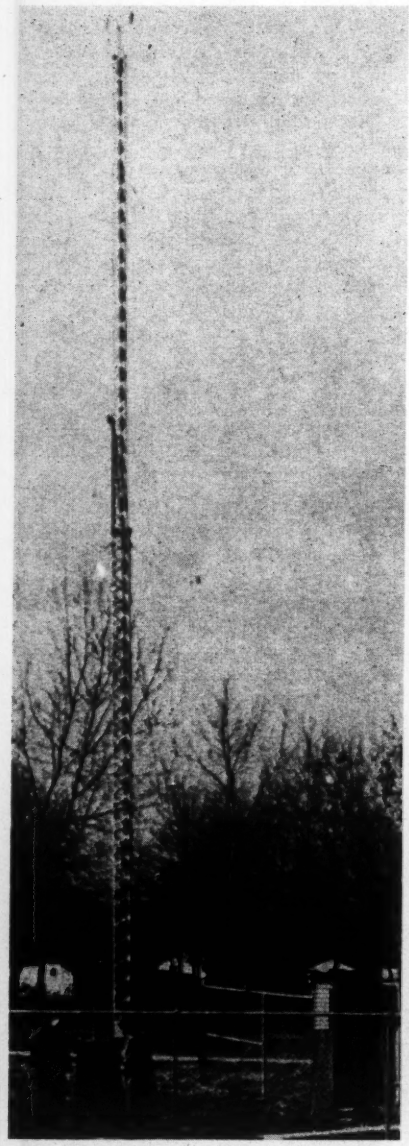

Fig. 4. View of a complete air sampling and meteorologic station.

Meteorologic Network

Considerable effort is being devoted to operation of a comprehensive meteorologic network by 2 staff meteorologists assigned by the Weather Bureau. There are 4 main meteorologic stations (Fig. 1), 2 of which coincide with stations No. 1 and 3 of the air sampling network.

The equipment at each of these stations consists of a 61-ft. aluminum and steel tower supporting a wind vane and anemometer wired to Beckman and Whitley recorders housed at the base of the tower. (Fig. 9) In addition, each of these stations has a recording hygrothermograph and wet- and dry-bulb thermometers housed in standard U. S. Weather Bureau shelters. Two more hygrothermograph recorders are situated at Iriquois Park, a high promontory on the south side of the city, and at Shawnee Park, in the extreme northwest section of the West End.

With the cooperation of the local broadcasting station (WHAS-TV), meteorologic instruments are being installed on a television tower. A wind vane will be installed at the 550 ft. level, and thermohms will be situated at the 50, 150, and 250 ft. levels. This equipment will be wired to continuous recorders housed

Fig. 5. Standard shelter employed in the air sampling network.

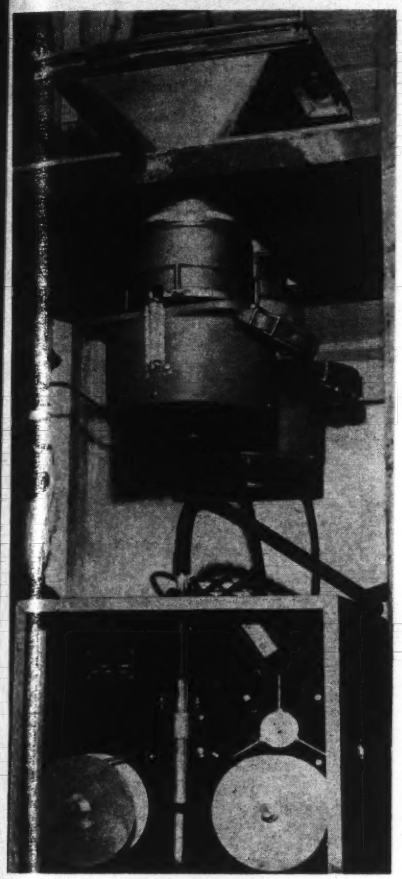

Fig. 6. Close-up of station showing high volume and filter tape samplers.

at the base of the tower. Tower instrumentation will permit vertical soundings of the atmosphere for measuring its degree of stability. In addition, soundings by wiresonde are contemplated. Addition of a mobile meteorologic station to the network is planned, to supplement the fixed stations as in the air sampling system.

Inventory of Air Pollution Sources

The third important phase of this study is an inventory of air pollution sources in Rubbertown. The approach consists of preliminary studies to become familiar with the plant processes, materials, mechanical equipment, waste products, and points of emission. Detailed stack sampling operations also are being carried out in cooperation with personnel from the U. S. Bureau of Mines and the Sanitary Engineering Center to determine the amount and chemical composition of solid and gaseous wastes. In addition, such physical characteristics as size, shape, and surface area of emitted aerosols are determined. The purpose of this phase of the study is

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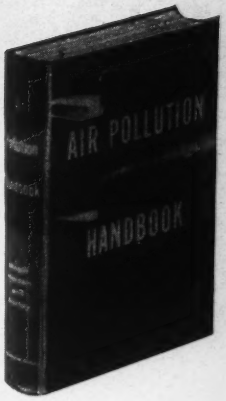

Here is the basic, one-volume sourcebook for authoritative facts and data on air pollution and its control. Written by a number of experts, the book is highly authoritative. It covers the theoretical, technical, and practical aspects—discusses causes, effects, and controls in chapters covering the science of air pollution, the effects on plants and animals, and the various corrective techniques. It tells exactly what is known about air pollution, how to apply what is known, and indicates where further research needs to be done.

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fumes and odors
smoke and suspended matter
theory of smog formation
types and locations of meteorological instruments
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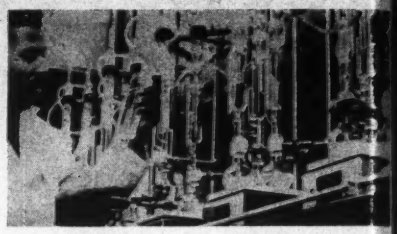

Fig. 7. Chemist using extraction equipment for determining organic content of air-borne particulates.

not only to learn the nature and rate of industrial discharges from Rubbertown, but also to compile an inventory of sources for use by local authorities in planning and evaluating regulatory measures. Tracer studies are planned for the future to determine range and influence of selected point sources.

Odor Survey

Another major phase of the study is a survey of the nature and origin of objectionable odors in the West End. The procedure includes a study of industrial operations and the collection and cataloging of samples of odorous material. Odor reference kits have been prepared for use by staff personnel and other cooperating individuals in making area surveys on a routine basis as well as during intense fumigations. Under development at the Sanitary Engineering Center is an olfactometer for quantification of odors.

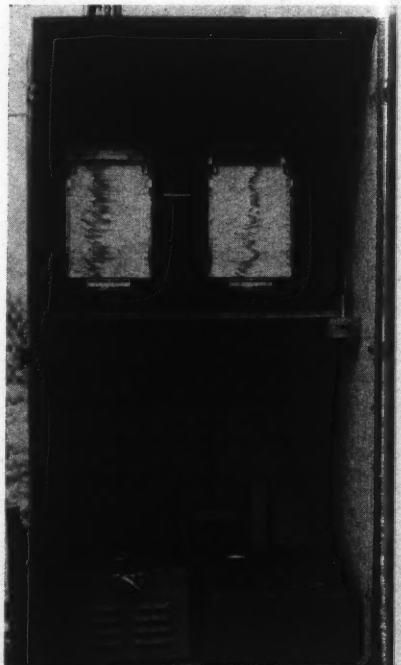

Fig. 9. Equipment for recording wind direction and speed.

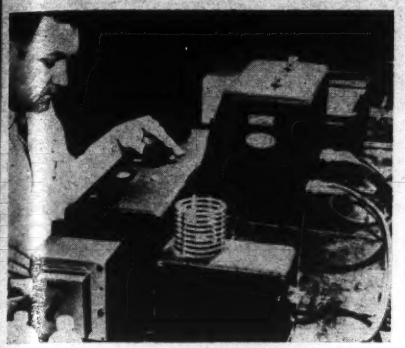

Fig. 8. Chemist using the flame photometer for analyzing air-borne particulates.

Trained Observer Program

A pilot study is underway to determine the nature, extent, and relative frequency of intense local fumigations resulting in objectionable odors, excessive dust, or related discomforting conditions among residents of the West End. This undertaking is exploratory and will depend largely on the cooperation of a corps of trained volunteer observers who are located in the West End. Using a daily recording form, each observer submits monthly reports of odor, dust, or irritating pollution incidents. Observers are provided with reference kits containing ten characteristic odors.

This activity represents not only a means to determine type, location, and frequency of annoying fumigations, but provides an alerting system for dispatching emergency air sampling crews and equipment to an affected area to study pollution at its peak levels.

Data Reduction

Early in the planning stages it became apparent the routine handling and reduction of the voluminous data and information collected during the study would constitute a formidable task. A working relationship was established with the analytical statistics group of the Sanitary Engineering Center to assist project analysts in this problem. In addition to advice and consultation in the design and planning of the survey, the Center assists in the reduction, analysis, and interpretation of data. Punch cards and electronic calculators are being used.

Public Relations

The field of air pollution is uniquely sensitive to public relations and opinion. This study gives cognizance to the importance of maintaining an adequate public information activity. Special attention is being given to development of a clear public understanding of the scope and general approach of the study, the participating organizations and staff, and amount and variety of detailed technical work required. The general public is being kept appraised of developments by successive news releases on what is being done and why. The ultimate aim is to produce a favorable climate of public opinion so final findings and conclusions will be of maximum use.

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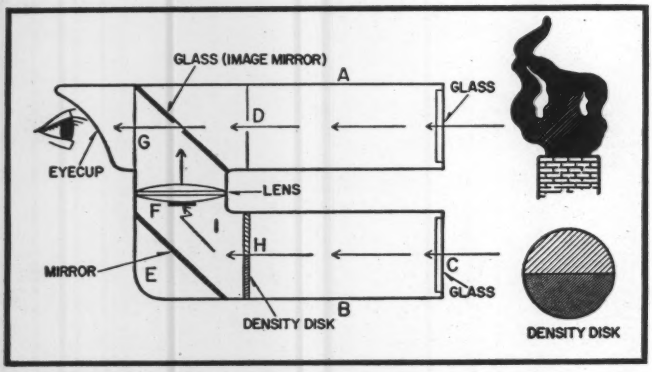

● *How it works*—Smoke picture fills field of vision through apertures C, D, and G. Light from area adjacent to stack is transmitted through reference disc, H, in barrel, B, to surface of mirror, E. Image of reference disc projects through lens, F, to image mirror where it is compared with smoke seen through apertures. Center of reference disc is blocked by opaque disc, I.

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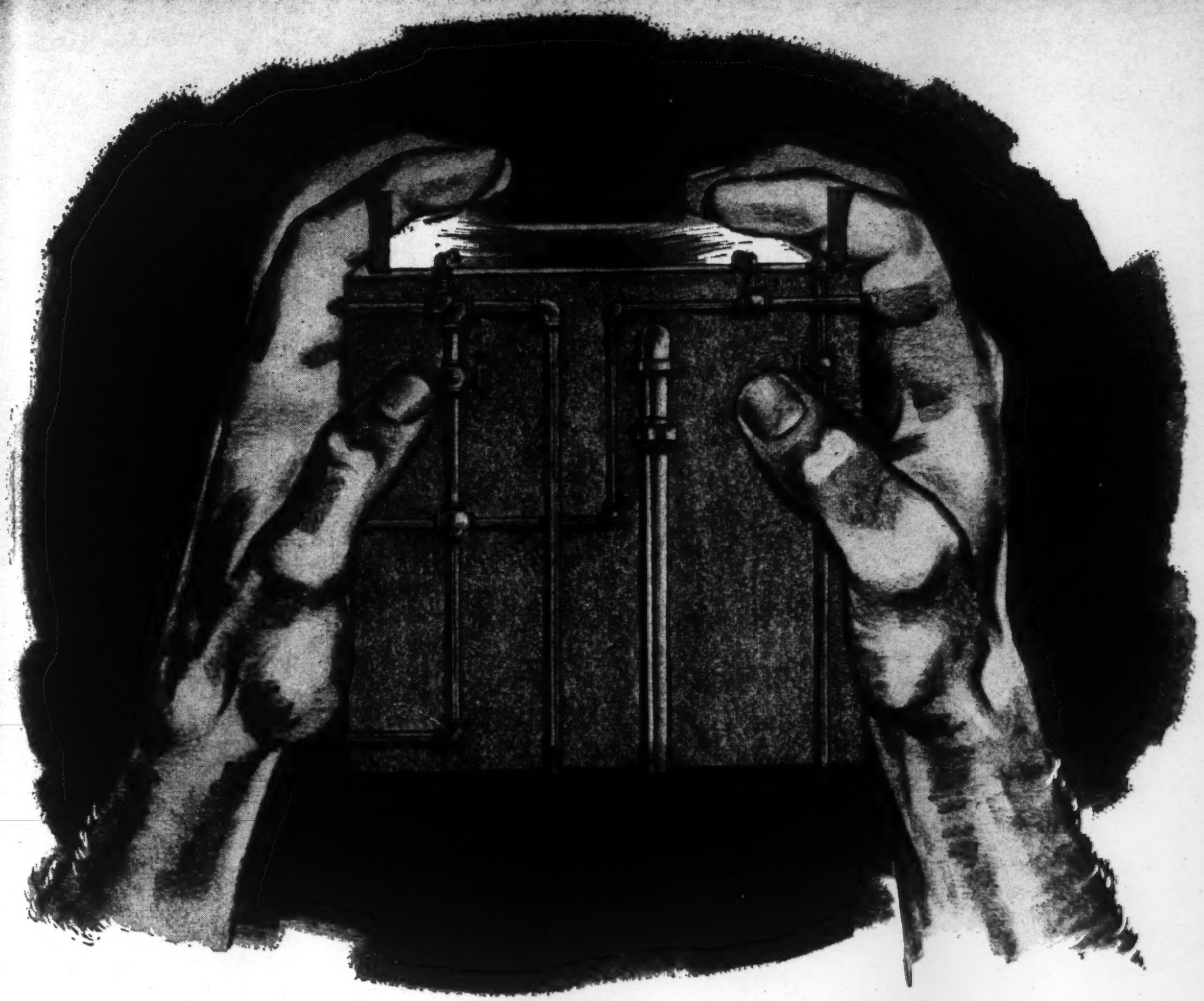

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ONE REASON WHY KOPPERS can make this promise is that Koppers builds the basic types of gas cleaning units. But obviously, that's not enough!

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How Koppers got that knowledge and experience is a story in itself. By building gas handling equipment for over seventy-five years. By handling coke gases in Koppers own plants for over forty-five years. By successfully solving gas cleaning problems in every industry where they are a headache . . . in plants of all sizes, with a wide variety of individual problems. So . . . when a Koppers engineer studies your specific problem, you know he has this wealth of experience to draw upon. It helps make him the best gas cleaning engineer in the business.

To drive your costs down even further in the solution of gas cleaning problems, Koppers carries on a never-ending research program . . . creating new gas cleaning techniques . . . finding out more and more about the properties and composition of materials that pollute the air. That's the job of Koppers' multi-million dollar research center at Verona, Pa.

Constant development of improved equipment and advanced design is the job of Koppers' Mechanical Development Laboratory at Baltimore. Backing up all this research is a sixty-year study by Koppers of current American and European gas cleaning techniques.

You profit by all this knowledge and research because it enables the Koppers engineer to recommend, without bias, the most efficient, most economical solution to your specific gas cleaning problem. If you have a problem, write to KOPPERS COMPANY, INC., Metal Products Division, Industrial Gas Cleaning Dept., 5611 Scott Street, Baltimore 3, Md.

Engineered Products sold with *Service*

KOPPERS

INDUSTRIAL GAS CLEANING EQUIPMENT

Whatever You Need, Koppers Makes It.

Koppers Electrostatic Precipitator. Koppers custom-designs Electrostatic Precipitators that eliminate "stack nuisance" . . . remove fly ash, acid mist, soot . . . recover high-value material.

Koppers New Cyclonic Type Dust Collectors. Produced after intensive study and experience, Koppers Mechanical Dust Collector provides maximum efficiency in mechanical dust removal.

Koppers Aeroturn Dust Collectors. Automatic pressure control and reverse-air-jet action provide high, continuous filtering. Clean air, reclaimed materials. Felt-type filters are more efficient; last longer.

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How the Steel Industry Is Fighting Air Pollution

When the public hears about dust and fume control it is often in terms of what has *not* been done. It is important that they should also know what *has* been done, because the record of the steel industry is one of the most progressive.

The purpose of this discussion is to give the executives the facts to prove this point.

Q. *First of all, how can you measure the progress of dust and fume control in the iron and steel industry?*

A. As you know, there are many ways to combat air pollution. Equipment and methods vary in effectiveness, but the industry agrees that electrical precipitators have the highest collection efficiencies. By keeping track of the demand for this high efficiency equipment over the years, we can get a good indication of the importance the industry places on dust and fume control and the progress they are making.

Q. *Do these figures show an increasing interest in this high efficiency equipment?*

A. Suppose we let the figures speak for themselves. Since 1945 precipitator capacity in the steel industry had a greater increase than in any previous ten year period. Precipitators handling about 6½ million cfm were installed during this period.

Q. *But can't you attribute this growth to the increase in steel-making capacity?*

A. Some of this growth is due to expanded production facilities, but that's just a part of it. For instance, iron and steel production has increased about 30% since 1945 — but precipitator capacity has increased about 130% during this same period.

Q. *In the old days, I guess precipitators were used primarily in blast furnaces, weren't they?*

A. That's right. The first one went into operation in 1930. Since then, 169 Research Cottrells have been ordered by the industry.

Q. *What about new applications?*

A. We have a number of new uses that have proven themselves on the job. Open hearths, for instance. In one installation, our precipitators reduced stack discharge to a little over 2 pounds per hour. That's quite a reduction when you consider that the discharge without a precipitator ranged from 75 to 245 pounds per hour.

Q. *I understand your Cottrells are used on some sintering machines now. Is this true?*

A. Yes, we have three in operation and more under construction.

Q. *How about scarfing machines?*

A. This is a recent application which has worked out very satisfactorily. Two precipitators are now in operation on this application.

Q. *Has anything been done on such problems as iron cupolas, electric furnaces, and ferromanganese blast furnaces?*

A. Yes. Installations have been made on all these problems.

Q. *How do you go about developing these new applications?*

A. We work very closely with our customers on these new projects. Our laboratory is a big help, and our 40 years of pilot plant experience plus over 2,000 precipitators give us the kind of experience that leads to the successful engineering of projects like these.

If you would like to have more information about these applications, or if you want to investigate the possibility of using precipitators on other equipment, our nearest representative will be glad to call on you.

RESEARCH-COTTRELL, INC.

A Wholly Owned Subsidiary of Research Corporation

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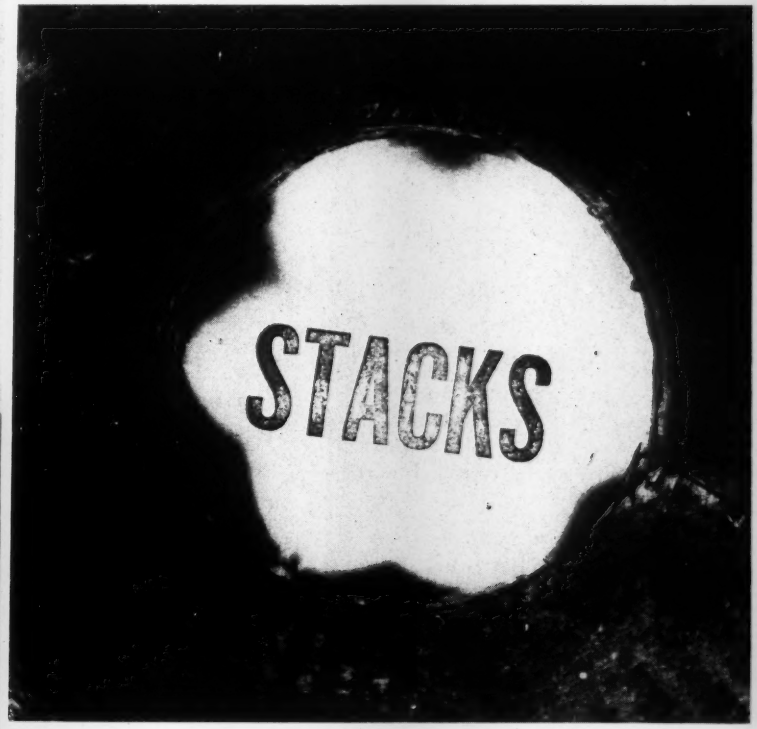

A Venturi Throat

(see page 219)